Development of Citric Acid Cross-Linked Starch for Controlled-Release Fertilizer (CRF)

by

Michelle Lee Huong Tiing

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons) Chemical

MAY 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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Dr. Zakaria B Man

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MICHELLE LEE HUONG TIING

ABSTRACT

The development of controlled-release fertilizers (CRF) have minimized plant nutrient loss uncontrolled by conventional fertilizers but still contain flaws in terms of the non-biodegradability and price of the coating material. This research aims to explore more on the potential of citric acid cross-linked starch as coating for CRFs. Since films developed from pure starch have weak mechanical properties, starch can be strengthened through chemical modifications such as cross-linking to produce value-added starch. Citric acid is used as a cross-link agent and its effectiveness is being studied. Preliminary preparation of starch solutions was done using deionized water, glycerol, native tapioca starch and citric acid of varying concentrations (0-30% w/w). Films were cast in an oven and were subjected to the water uptake test and swelling/disintegration test. The cross-linked film squares immersed in water for the swelling/disintegration test appeared to be intact for up to one week whereas the non-cross-linked film square degraded early in the test. As for the water uptake test, the starch films containing a higher amount of citric acid exhibited a lower percentage water uptake as compared to starch films containing a lower amount of citric acid. This phenomenon is attributed to the extent of cross-linking within the starch molecular structure which may encourage or inhibit the entry of water molecules. Urea prills coated with the cross-linked starch solution were viewed under a scanning electron microscope. The images show that the coating process was successfully done, with the coating adhering to the surface of the urea prill, although not very homogenously.

ACKNOWLEDGEMENTS

First and foremost, I offer my thanks to God, of whom without, I would not have the wisdom, ability and strength to carry out this entire Final Year Project.

I would like to express my greatest gratitude to Dr. Zakaria B Man, for his endless guidance and support in assisting me throughout the Final Year Project. He has spent much time and effort in giving valuable advice from his vast knowledge on the subject in order for me to complete this research smoothly. The objectives of this project would not have been achieved completely and timely without his expertise.

Besides that, I also extend my appreciation to Miss Ariyanti Sarwono, a PhD student assigned to assist me by Dr. Zakaria B Man. She has been of great help especially with laboratory works. She assisted me in preparing my samples and helped me understand the theoretical aspect of my project as well. Additionally, I would like to thank the lab technicians who have been very cooperative throughout the course of my work. This research project would not have been possible without the facilities provided by Universiti Teknologi PETRONAS.

Lastly, I would like to convey my thanks to my family, who have given me never-ending moral support from the beginning till the end of this research project.

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ABBREVIATIONS AND NOMENCLATURES

CRF	Controlled-Release Fertilizer
FAO	Food and Agriculture Organization of the United Nations
FUE	Fertilizer Use Efficiency
FYP	Final Year Project
PCL	Polycaprolactone
PLA	Polylactide
SCBP	Starch-Based Completely Biodegradable Polymer
SEM	Scanning Electron Microscopy
TPS	Thermoplastic Starch

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Plants require several chemical elements in order to thrive. Three of these elements, carbon, hydrogen and oxygen, are abundant in supply and can be obtained from surrounding air and water. There are also three primary macronutrients essential for plant consumption: nitrogen, phosphorus and potassium, which are elements naturally found in soil from the decay of dead plants. Most soil types are able to cater to a plant's nutrition requirements for a complete life cycle. However, shortage of nutrients will result in poor plant growth. Plant nutrient deficiencies have brought about the application of fertilizers, benefitting the agriculture industry in terms of macronutrient supply for plants and resulting in improved crop yields. Different types of organic and inorganic fertilizers of both natural and synthetic origins respectively have been developed over the years. Conventional fertilizers consist of water soluble materials such as urea. In order to curb nutrient loss due to surface runoff and vaporization, fertilizers are coated to produce controlled-release fertilizers (CRFs). CRF coating materials are usually made of synthetic polymers which are non-biodegradable. When the CRF is exhausted, the polymeric remains can pose a risk to the environment. Research has been done on using biopolymers such as starch as an alternative for CRF coating. Starch may be a biodegradable and abundant resource, but it is also soluble in water, making it slightly unfit to coat CRFs. Cross-linking is a method employed to develop more satisfactory properties of starch. Even so, most cross-link agents used to modify starch are relatively toxic, and may not result in the desired improvement of properties.

1.2 PROBLEM STATEMENT

1. Current CRF coating materials are non-biodegradable and expensive.
2. Biopolymers such as starch exhibit strong hydrophilic characteristics (high water sensitivity) and poor physicochemical properties, rendering them unsuitable for CRF coating.

1.3 OBJECTIVES

The objective of this study is to evaluate the effectiveness of citric acid as a cross-link agent used to modify native tapioca starch. The variable being analysed is the amount of citric acid used to cross-link the starch. Ultimately, this research aims to determine the relationship between the **amount of citric acid** used for cross-linking and the **physicochemical properties** of the resulting cross-linked starch films to be used for CRF coating.

1.4 SCOPE OF STUDY

In this study, the parameter under investigation is the quantity of citric acid used for tapioca starch cross-linking. Subsequently, the chemical structure microscopy and water uptake of the cross-linked starches are studied.

1.5 RELEVANCY AND FEASIBILITY

The research on CRF development is relevant to our society in terms of agricultural support with the increasing worldwide demand of food. This research also moves in line with rising global efforts to implement green technology in all industries.

The study plan in Chapter 3 shows the feasibility of conducting this research with respect to the FYP I and FYP II timelines.

CHAPTER 2

LITERATURE REVIEW

2.1 CONTROLLED-RELEASE FERTILIZERS

Fertilizers play an important role in the agricultural sector in terms of plant nutrient uptake to sustain crop production consistent with the growing global population. Nevertheless, when applied in conventional forms, the fertilizer dose recovered by plants has been reported to only reach an estimated 30-50% (Prasad, Rajale, & Lakhdive, 1971). Low efficiency of plant nutrient uptake may be caused by vaporization, immobilization, denitrification, and also leaching, which is especially true in sandy soil subject to severe irrigation (Hanafi, Eltaib, & Ahmad, 2000). These setbacks initiated the research on controlled-release technology to be integrated in fertilizer use with the aim of reducing nutrient deficiencies in plants. This research resulted in the coating of fertilizers to produce controlled-release fertilizers (CRFs).

Figure 2.1: Conventional Fertilizer Granules

CRFs are generally used for the fertility management of soil in order to meet the physiological requirements of plants (Hanafi *et al.*, 2000). CRFs are made by coating existing water-soluble fertilizer granules with materials exhibiting suitable coating properties, therefore reducing their dissolution rate. Fertilizer release occurs through diffusion, and its rate is controlled at effective levels in the soil, supplying plants with nutrients when necessary.

Figure 2.2: KAMILA, a Type of CRF Recently Developed in Malaysia

Previously-developed CRFs have been reported to be coated with sulfur (Rindt, Blouin, & Getsinger, 1968) and synthetic polymers such as polyethylene, polystyrene and polycarbonate (Salman, 1988), polyvinyl chloride (Hanafi *et al.*, 2000), and biopols (Devassine, Henry, Guerin, & Briand, 2002). Yan, Jin, He and Liang (2008) studied the fertilizer use efficiency (FUE) of both polymer-coated CRFs and common fertilizers and later reported that CRF use resulted in a higher crop yield (46.6%) as compared to common fertilizer use (15%). Although the use of polymer-coated CRFs presents satisfactory outcomes, they are non-biodegradable, hence posing a threat to the environment. Inorganic fertilizer use has increased nutrient pollution over the past years and disrupted ecosystem functioning (Mozumder & Berrens, 2007). Moreover, the development of biopolymer-coated CRFs is scarce, though not unheard of.

2.2 CROSS-LINKED TAPIOCA STARCH AS FERTILIZER COATING

Starch, as a naturally-occurring biopolymer, is a major carbohydrate reserve in plants. It is a polysaccharide comprising amylose (linear) and amylopectin (branched). Considering that it is economical, biodegradable and abundant in staple food such as maize, potatoes, wheat, and cassava (tapioca), starch can be deemed as one of the most practical biopolymers for fertilizer coating.

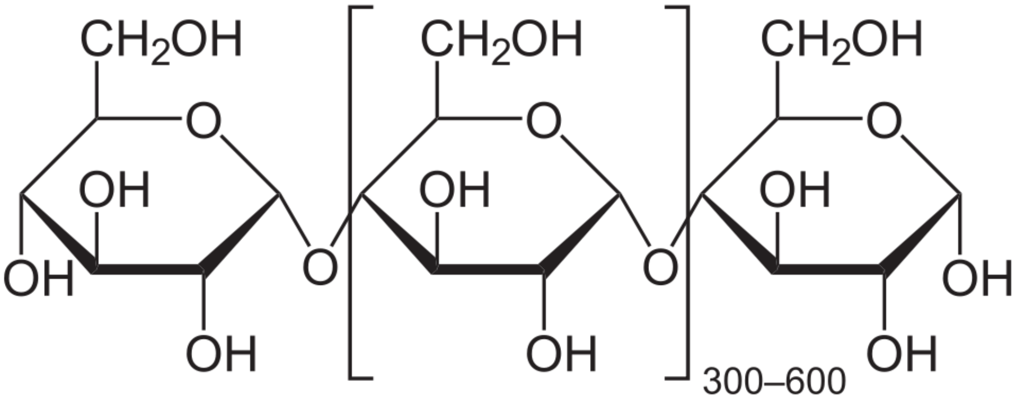


Figure 2.3: Structure of Amylose Molecule

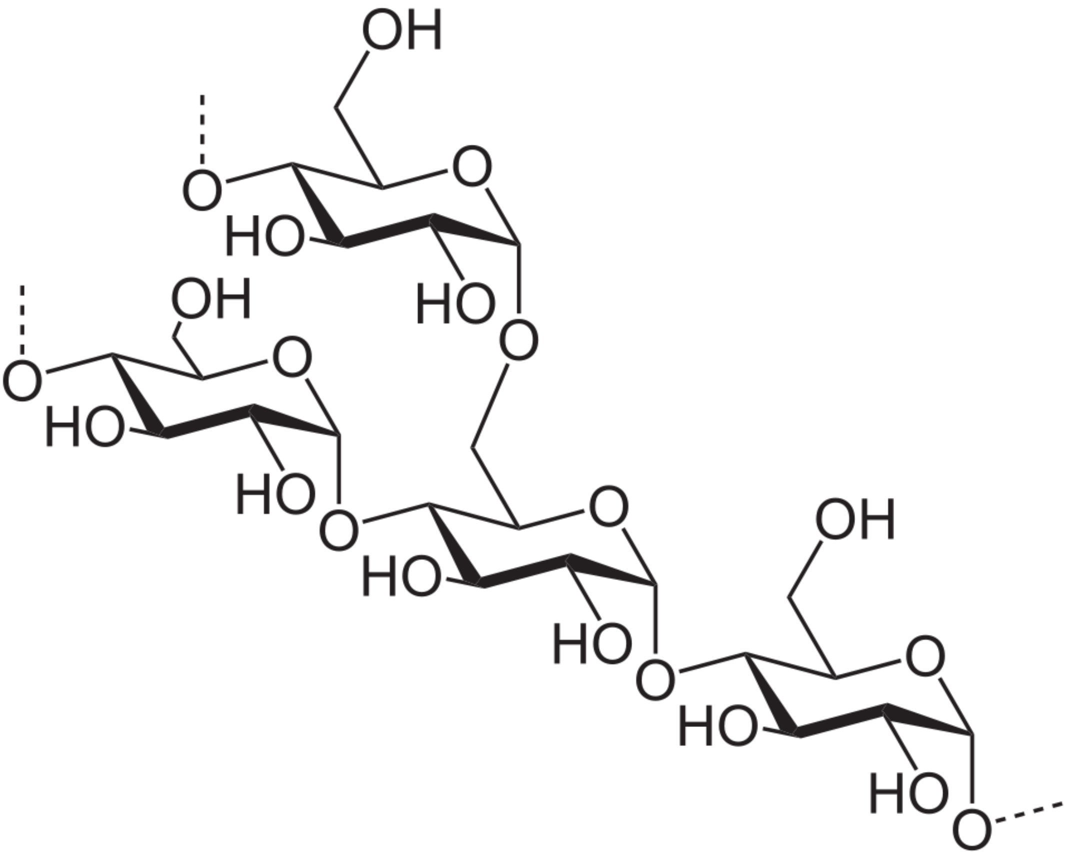


Figure 2.4: Structure of Amylopectin Molecule

Various types of starch have been subjected to cross-linking, such as corn/maize starch (Garg & Jana, 2007; Koo, Lee, & Lee, 2010), wheat starch (Hung & Morita, 2005) and sago starch (Singh & Nath, 2012). Among the starches extracted from different crops, tapioca starch appears to be less prominent in fertilizer development.

Figure 2.5: Tapioca Root from which Tapioca Starch is Extracted

Comparatively, tapioca is a highly competitive crop. It is the staple food of rural people in Africa, Asia and Latin America. The Food and Agriculture Organization of the United Nations [FAO] (2006) stated that the export prices of tapioca starch have remained lower than those of maize, potato and wheat starches over the years. Tapioca plants are capable of giving high yields, exhibiting a tolerance to drought, and offering flexibility in planting and harvesting. Apart from being processed into food, tapioca starch is also used as a raw material in various non-food applications such as the textile, pharmaceutical, adhesive and cosmetic industries. Employing tapioca starch in fertilizer production will open new markets and further enhance the booming starch business by supporting local farmers and developing rural economies. Above all, tapioca starch is capable of substituting maize, wheat and rice starch in terms of functionality (Tonukari, 2004). While tapioca starch is being mass-produced for industrial use in order to meet the increasing global demand, it is certain that tapioca starch has an excellent potential in fertilizer development.

Recent non-food industrial applications call for starch to undergo value-addition to achieve specific functional characteristics. Lu, Xiao and Xu (2009) found that starch can be physically blended with synthetic biodegradable polymers and biopolymers to produce starch-based completely biodegradable polymers (SCBPs). They compared the properties of thermoplastic starch/polylactide (TPS/PLA) blends and thermoplastic starch/polycaprolactone (TPS/PCL) blends with those of native starch and concluded that some form of improvement is shown in the mechanical properties of the composites, especially with the TPS/PCL blend. However, the incompatibility between starch and synthetic polymers is prominent as there is poor interfacial interaction between starch granules and the polymer. This requires a need to introduce plasticizers to the process and/or allow the gelatinization of starch to boost interfacial affinity, which complicates the blending process.

An alternative method of starch modification is cross-linking; a method intended to stabilize and strengthen starch by adding chemical bonds in a granule (Singh & Nath, 2012). Cross-linking involves chemical reactions between a polymer and a cross-link agent. By cross-linking, the internal grain structure of starch is strengthened, increasing its solidity.

Pharmaceutical researchers have studied the controlled-release behaviour of bioactive molecules extensively over the years. As a natural polymer, starch has been modified and applied in various areas of controlled-release coatings for biopharmaceutical applications. Atyabi, Manoochehri, Moghadam and Dinarvand (2006) in their work cross-linked starch microspheres with epichlorhydrine to be used for enzymatic-controlled colonic drug delivery. They later reinforced the epichlorhydrine cross-linked microspheres with formaldehyde and glutaraldehyde as secondary cross-link agents. Glutaraldehyde proved to be a more effective cross-link agent as compared to epichlorhydrine and formaldehyde as it gave the starch microspheres the smoothest surface and a slower drug release rate. The study showed that particle size, swelling ratio and release characteristics of the microspheres could be controlled by varying the type and concentration of the cross-link agent and the cross-linking time. Moreover, the enzymatic degradation of cross-linked starch microspheres (shown by the drug release studies) supports the concept of CRF development whereby the CRF releases nutrients after its coating undergoes controlled, gradual degradation depending on soil moisture and temperature.

2.3 CITRIC ACID AS CROSS-LINK AGENT

Citric acid is a carboxylic acid with three carboxyl groups found primarily in citrus fruits.

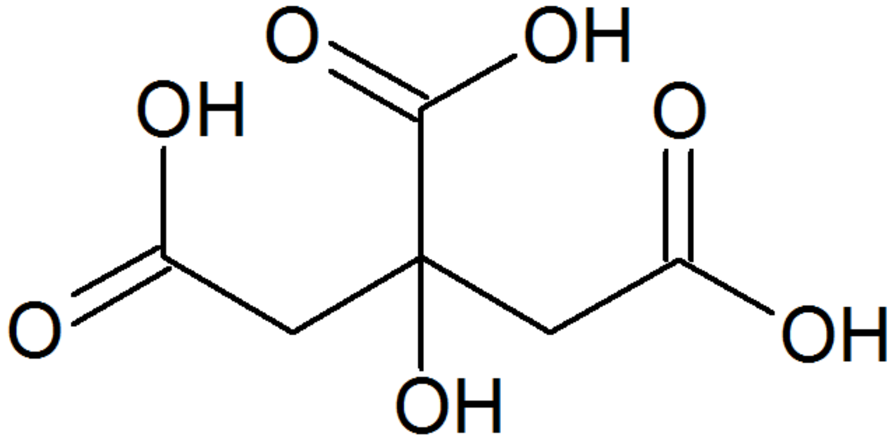


Figure 2.6: Structure of Citric Acid

Citric acid is preferable in industrial applications as it poses little to no threat to the environment. Citric acid has also been proven to be convenient for cross-linking as it can be obtained through fermentation and is non-toxic (Reddy & Yang, 2010). In cross-linking processes, reactions between the carboxyl groups of citric acid and the hydroxyl groups of starch are able to improve the performance of starch. Ma, Chang, Yu, and Stumborg (2009) introduced citric acid-modified starch to thermoplastic pea starch composites and came to a conclusion that the citric-acid modified starch improved the tensile strength and water vapour barrier properties but decreased the thermal stability of the composites. This differs from the findings of Shi *et al.* (2008), whereby the increase in citric acid concentration increased the thermal stability of polyvinyl alcohol/starch films.

With relevance to CRF coating, Reddy and Yang (2010) have initiated a study on citric acid cross-linked starch films with the intention of improving the mechanical properties and decreasing the dissolution rate of starch in water. Their study showed that the cross-linked starch films exhibit better thermal stability, lower weight loss in formic acid, and lower water vapour permeability without major alterations in their morphology and crystallinity.

Besides further enhancing the work of Reddy and Yang (2010), this research aims to optimize and apply any findings in CRF development.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 RESEARCH METHODOLOGY AND PROJECT ACTIVITIES

The basic experimental approach to this research is shown below.

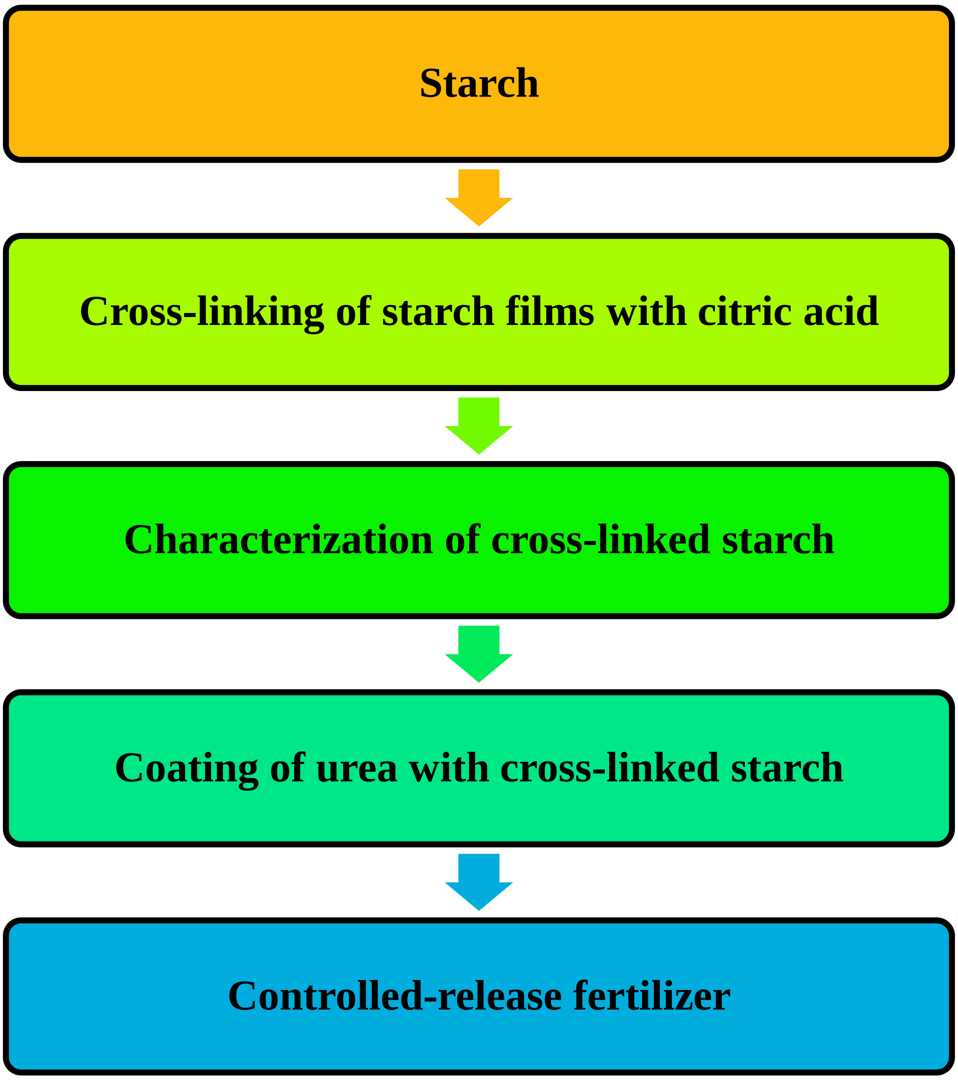


Figure 3.1: Research Schematic Flow

3.1.1 Preparation of Cross-linked Starch Films

1. 5% w/v of native tapioca starch, 20% w/w of glycerol and two drops of food colouring are mixed in 200 mL of deionized water, according to ***Table 3.1***.
2. The starch dispersion is heated to 80°C in a water bath while being stirred with a magnetic stirrer at 220 rpm (as shown in ***Figure 3.3*** on the following page).
3. The temperature of the starch dispersion is maintained at 80°C for 30 minutes and then left to cool to room temperature.
4. Citric acid powder (according to ***Table 3.1***) is dissolved in the starch dispersion and stirred for 10 minutes at 100 rpm.
5. The starch solution is poured into casting containers (each holding 40 g of starch solution) and left to dry for 24 hours, 72 hours and 240 hours (according to ***Table 3.2***) at 40°C in a hot air oven.
6. The cast films are peeled from the casting containers and cut into squares 3 cm × 3 cm in size.
7. The film squares are treated in a hot air oven at 105°C for 10 minutes while the remainder of the film is stored in airtight containers with silica gel for future use.

Table 3.1: Composition of Cross-linked Starch Films

Sample	Composition				
	Deionized Water (mL)	**5% w/v Starch (g)**	**20% w/v Glycerol (g)**	**Citric Acid (% w/w)**	**Citric Acid (g)**
SCA0	200	10	2	0	0
SCA10	200	10	2	10	1.0
SCA15	200	10	2	15	1.5
SCA20	200	10	2	20	2.0
SCA25	200	10	2	25	2.5
SCA30	200	10	2	30	3.0

Table 3.2: Naming of Starch Samples

Name	Description
24-hour samples	Films cast for 24 hours
72-hour samples	Films cast for 72 hours
240-hour samples	Films cast for 240 hours

Figure 3.2 below summarizes the experimental parameters for the preparation of cross-linked starch films.

Solution mixing (starch + glycerol)	
Temperature: 80°C	Duration: 30 mins
Addition of citric acid to solution	
Room temperature	Duration: 10 mins
Film casting	
Temperature: 40°C	Duration: 24 h, 72 h, 240 h
Film curing	
Temperature: 105°C	Duration: 10 mins

Figure 3.2: Graphical Representation of Preparation of Cross-linked Starch Films

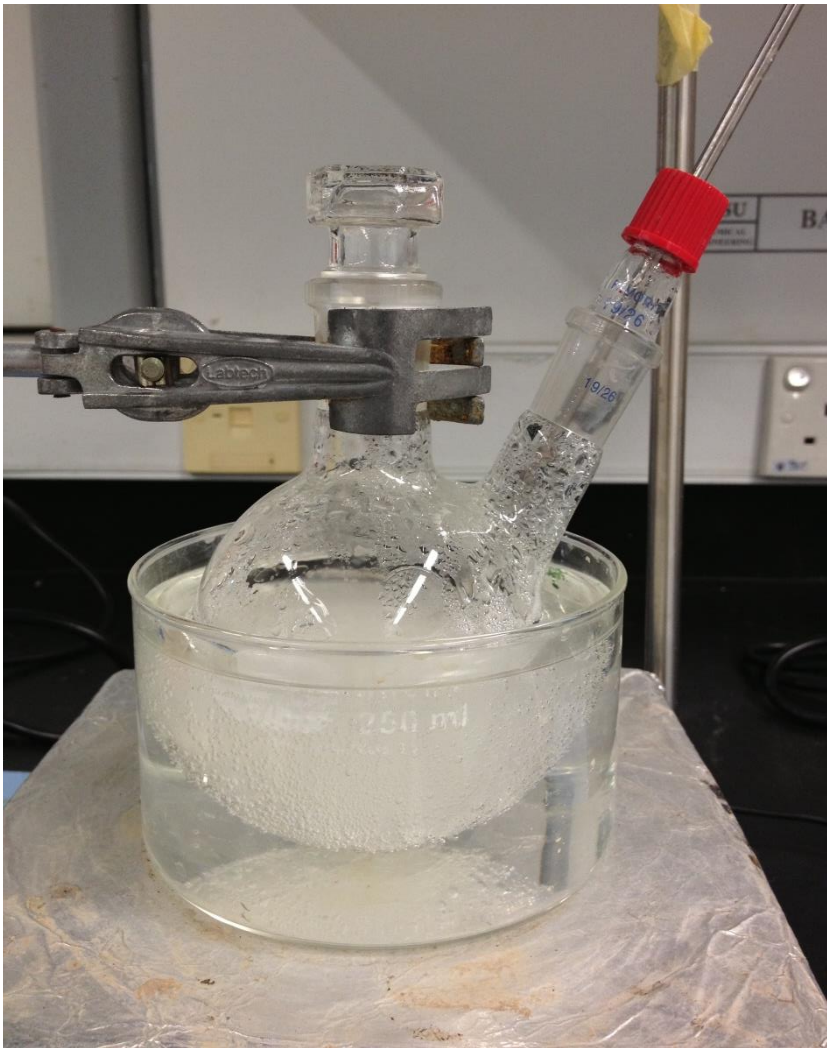
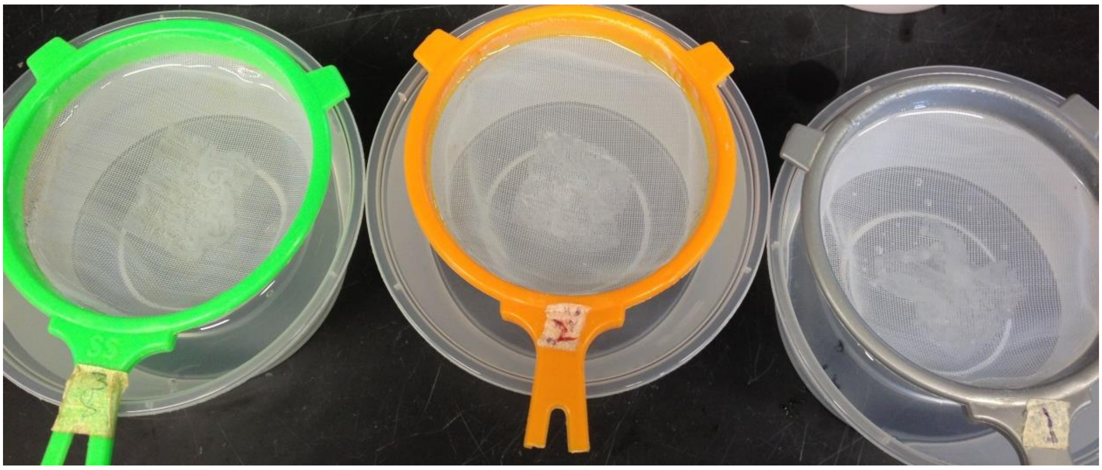


Figure 3.3: Apparatus Set Up for the Heating of Starch Dispersion

3.1.2 Water Uptake Test

1. The cured film squares are first weighed to obtain their initial weights.
2. Each film square is placed into a small strainer and fully immersed in a container of deionized water (as shown in ***Figure 3.4*** below).
3. Every hour, the film square is lightly dried and weighed.
4. The weights of each film square are obtained over a few hours (or days) and recorded in a table. The water uptake is calculated and plotted in a graph.

(a) Placement of film square in strainer



(b) Immersion of film square and strainer in water

Figure 3.4: Set Up for Water Uptake Test

3.1.3 Swelling/Disintegration Test

1. The cured film squares are each immersed in deionized water in a petri dish or round plastic container (as shown in ***Figure 3.5*** below).
2. Pictures of the film squares are taken every hour (or every day) to observe the swelling behaviour and determine the duration of which the film squares begin to disintegrate.

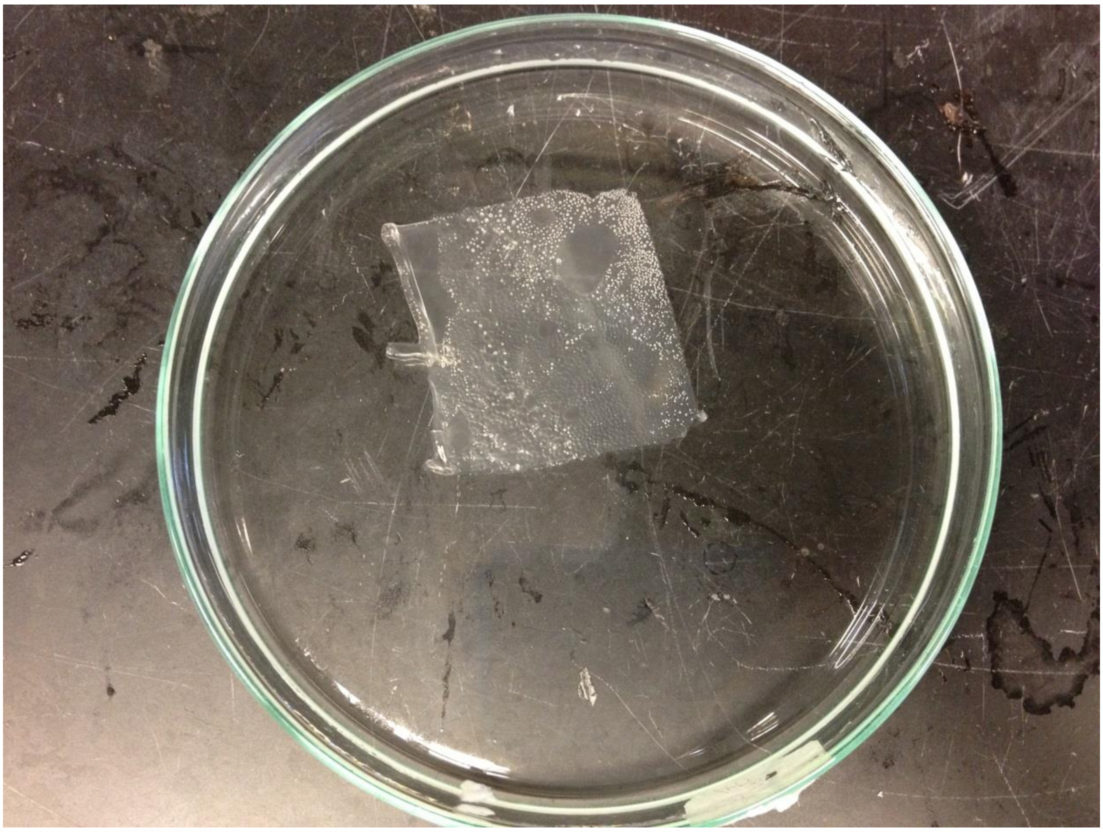


Figure 3.5: Set Up for Swelling/Disintegration Test in Petri Dish

3.1.4 Coating of Urea Prills

1. Urea prills are coated using the dip-coating method.
2. Raw urea prills (as shown in ***Figure 3.6***) are dipped into the starch solutions each containing different amounts of citric acid.
3. The coated urea prills are then left to dry in a hot air oven at 40°C for 4 hours. Steps 2-3 are repeated two more times.
4. After the coatings of the urea prills have been cast, the urea prills are treated in a hot air oven at 105°C for 10 minutes.

Figure 3.6: Raw Urea Prills

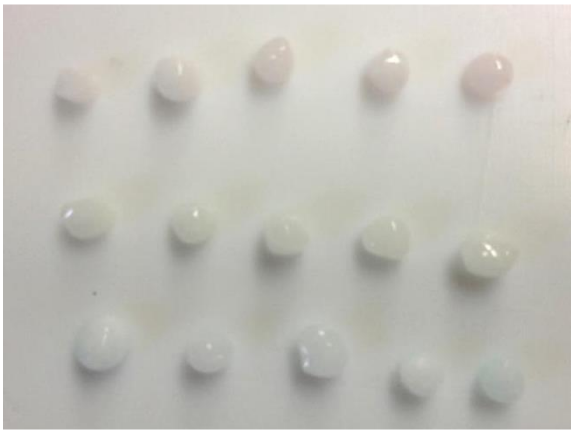


Figure 3.7: Coated Urea Prills

3.1.5 Scanning Electron Microscopy (SEM)

(The scanning electron microscope was outsourced, using the coated urea prills as prepared in **Section 3.1.4**. *Images were captured using a fully-coated urea prill and coated urea prill dissected in half.)*

3.2 FYP I STUDY PLAN

Table 3.3: FYP I Gantt Chart

No.	Week / Activity	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	■	■						**Mid-semester break**							
2	Final Year Project I Briefing	■														
3	Preliminary Research Work		■	■	■	■										
4	Literature Review and Critical Analysis				■	■	■	■								
5	Submission of Extended Proposal							■								
6	Preparation for Proposal Defence							■		■						
7	Proposal Defence Presentation									●						
8	Commencement of Project Work									■	■	■	■	■		
9	Preparation of Interim Report												■	■		
10	Submission of Interim Draft Report														●	
11	Submission of Interim Report															●

■ Process ● Milestone

<u>FYP I Key Milestones</u>

6 March 2013: Proposal Defence Presentation

11 April 2013: Submission of Interim Draft Report

22 April 2013: Submission of Interim Report

3.3 FYP II STUDY PLAN

Table 3.4: FYP II Gantt Chart

No.	Activity \ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Continuation of Project Work	■	■	■	■	■	■	■									
2	Submission of Progress Report									●							
3	Continuation of Project Work									■	■	■	■	■			
4	Pre-SEDEX												●				
5	Submission of Draft Report													●			
6	Submission of Soft Bound Dissertation								Mid-semester break						●		
7	Submission of Technical Paper														●		
8	Preparation for Oral Presentation													■	■		
9	Oral Presentation															●	
10	Finalization of Final Project Dissertation															■	■
11	Submission of Final Project Dissertation																●

■ Process ● Milestone

<u>FYP II Key Milestones</u>

8 July 2013: Submission of Progress Report

31 July 2013: Pre-SEDEX

5 August 2013: Submission of Draft Report

15 August 2013: Submission of Soft Bound Dissertation and Technical Paper

27 August 2013: Oral Presentation

30 September 2013: Submission of Final Project Dissertation

CHAPTER 4

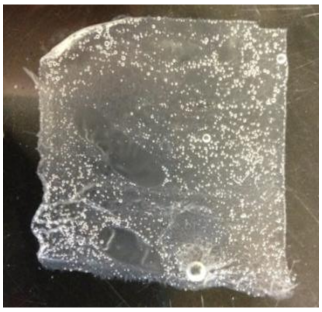
RESULTS AND DISCUSSION

The initial experimental procedure employed in FYP I yielded unsatisfactory results. Therefore, the procedure was reviewed and modifications were made based on updated literature to improve the quality of the starch films.

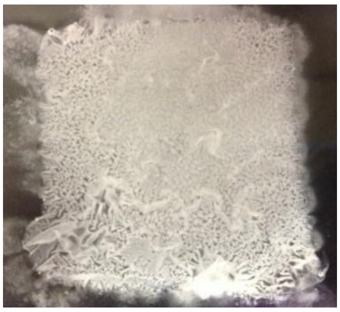
4.1 RESULTS AND DISCUSSION FOR CROSS-LINKED STARCH FILMS PREPARED ACCORDING TO FYP I EXPERIMENTAL PROCEDURE

The first experimental procedure required the addition of citric acid when the starch solution is cooled to **60°C** after heating and the curing duration was to be determined at **130°C**. When being subjected to the swelling/disintegration and water uptake tests, the films broke down and dissolved in water. For the purpose of discussion, test results for SCA10 films will be used to represent data for all other films.

4.1.1 Swelling/Disintegration Test



(a) Upon immersion



(b) 4 hours of immersion

Figure 4.1: SCA10 Swelling/Disintegration Test

Figure 4.1 shows an SCA10 film square (cured at 130°C for 2 hours) being immersed in water for 4 hours. It is evident that the film disintegrates in water within a very short period of time. This is not a desirable characteristic of CRF coatings.

4.1.2 Water Uptake Test

Table 4.1: SCA10 Water Uptake Data

Initial weight of film = 0.2964 g				
Duration (hours)	1	2	3	4
Weight of film (g)	**1.5025**	**0.6245**	**0.5036**	**0.3645**
Water uptake (g)	1.2061	0.3281	0.2072	0.0681
Water uptake (%)	406.92	110.70	69.91	22.98

The water uptake data in ***Table 4.1*** shows a decrease in film weight during immersion in water, which then inhibits water uptake in the films. This is because the films dissolved in water over time, causing a significant drop in weight.

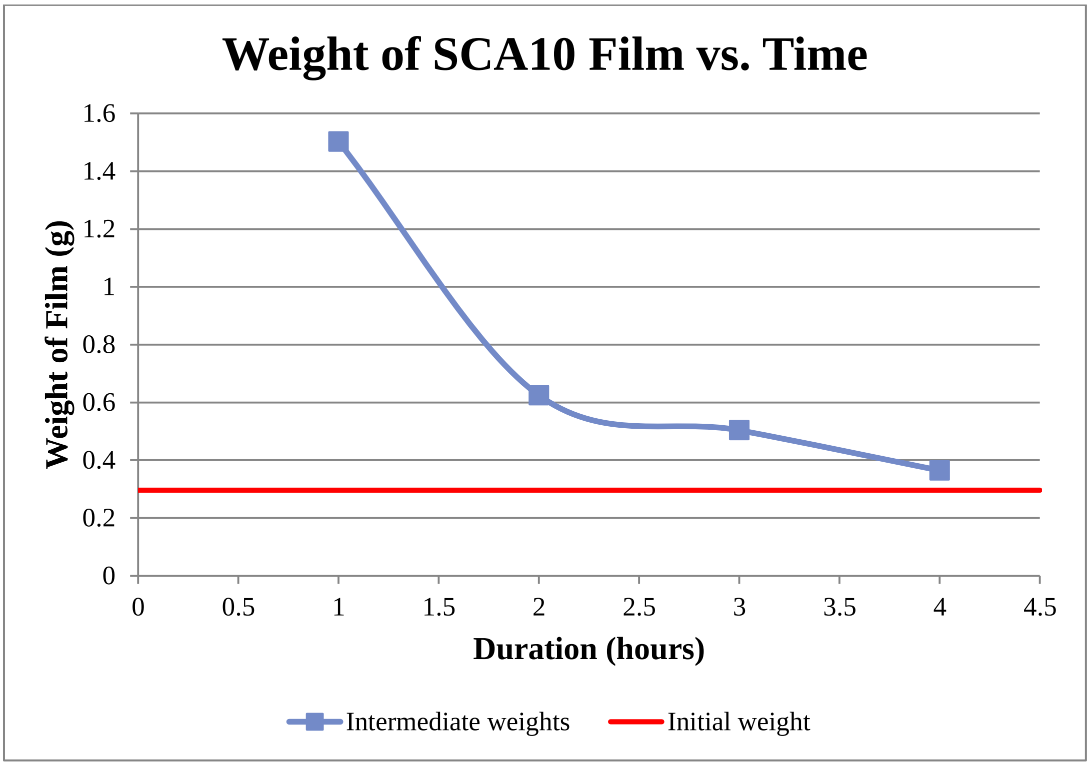


Figure 4.2: Graph of SCA10 Film Weight over Time

Figure 4.2 shows the decline in film weight over time. It is important to note that approaching 4.5 hours of immersion, almost all the film had dissolved.

Since all films exhibited similar results in the swelling/disintegration and water uptake tests as discussed in ***Sections 4.1.1 and 4.2.2***, this batch of films was deemed unsuitable for CRF coating as the films were unable to withstand contact with water. Consequently, the experimental procedure was revised.

4.1.3 Modifications on Experimental Procedure

Some modifications were made to the experiment parameters in line with trial and error occurrences and cited literature, as summarized in ***Table 4.2*** below.

Table 4.2: Modifications Applied to Experimental Procedure

Initial Method	Modification	Justification
No food colouring added to starch solution	**Food colouring** added to starch solution: SCA10 – red SCA15 – yellow SCA20 – green SCA25 – blue SCA30 – violet	Different colours help to distinguish between starch films
Citric acid added when starch solution is cooled to **60°C**	Citric acid added when starch solution is cooled to **room temperature**	The temperature is lowered based on the work of Menzel *et al.* (2013)
Casting temperature: **50°C**	Casting temperature: **40°C**	When cast at 50°C, some films cracked and were very brittle (refer to ***Figure 4.3***), possibly due to the rapid evaporation of water
Curing temperature: **130°C**	Curing temperature: **105°C**	The curing temperature is lowered based on the work of Menzel *et al.* (2013)
Curing duration: **1 h, 2 h, 3 h**	Curing duration: **10 min**	Prolonged curing damages the starch molecules (Reddy & Yang, 2010), resulting in weak films

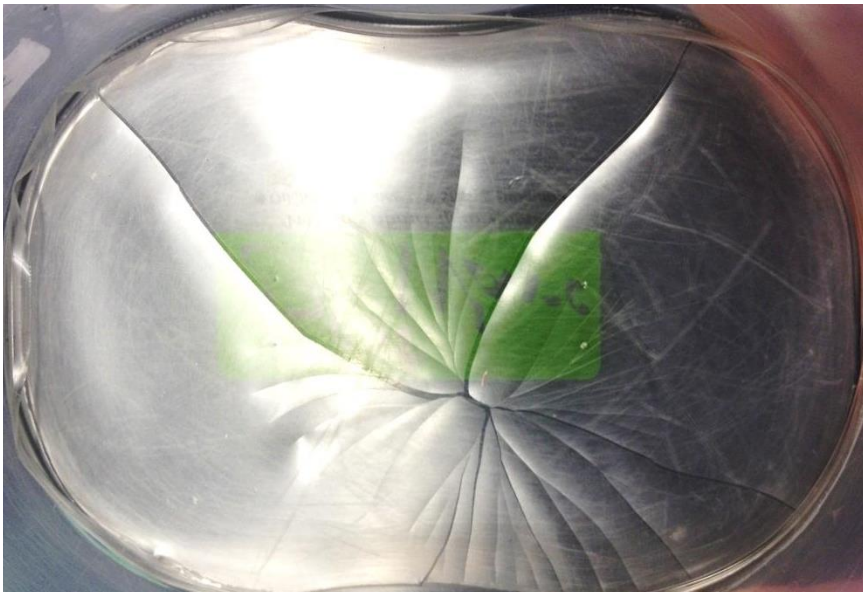
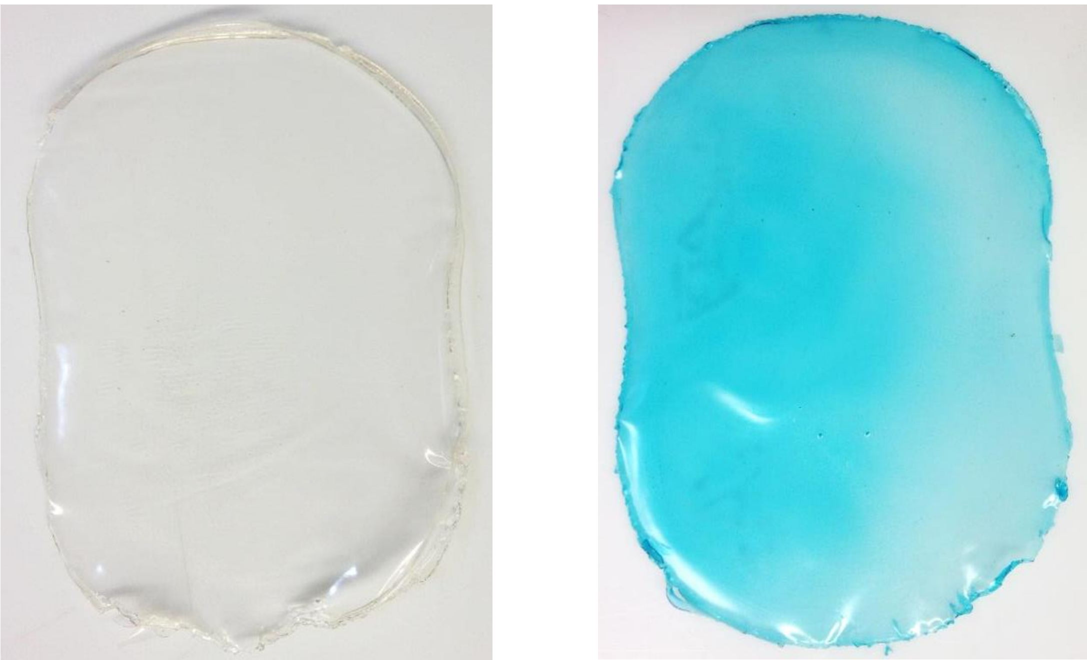


Figure 4.3: Cracked Film

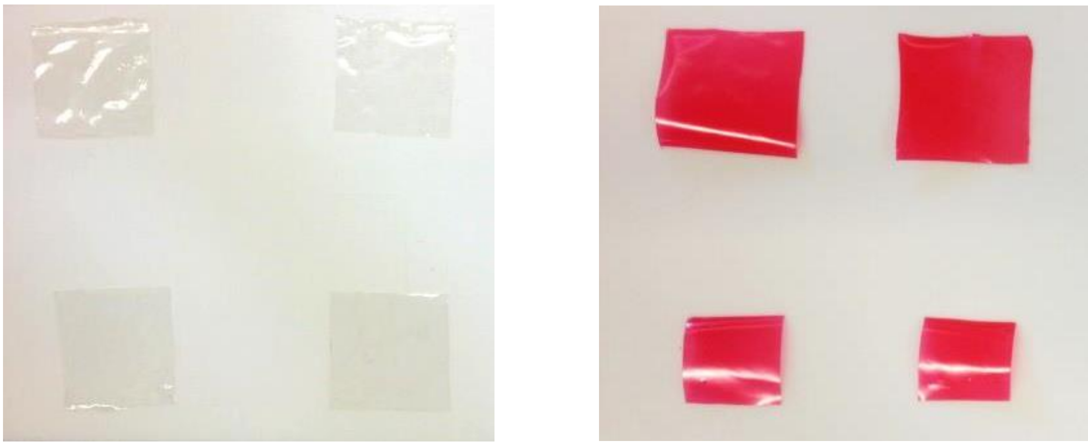
4.2 RESULTS FOR CROSS-LINKED STARCH FILMS PREPARED ACCORDING TO UPDATED EXPERIMENTAL PROCEDURE

A new batch of cross-linked starch films was prepared according to the updated parameters. These films were easier to handle as compared to those from the previous batch. The cast films were peeled off the casting containers without much difficulty and felt more solid than the previous films, which were very fragile. Also, the food colouring helped to improve identification of the many starch films, as shown in ***Figures 4.4 and 4.5*** below.



(a) Without food colouring (b) With blue food colouring

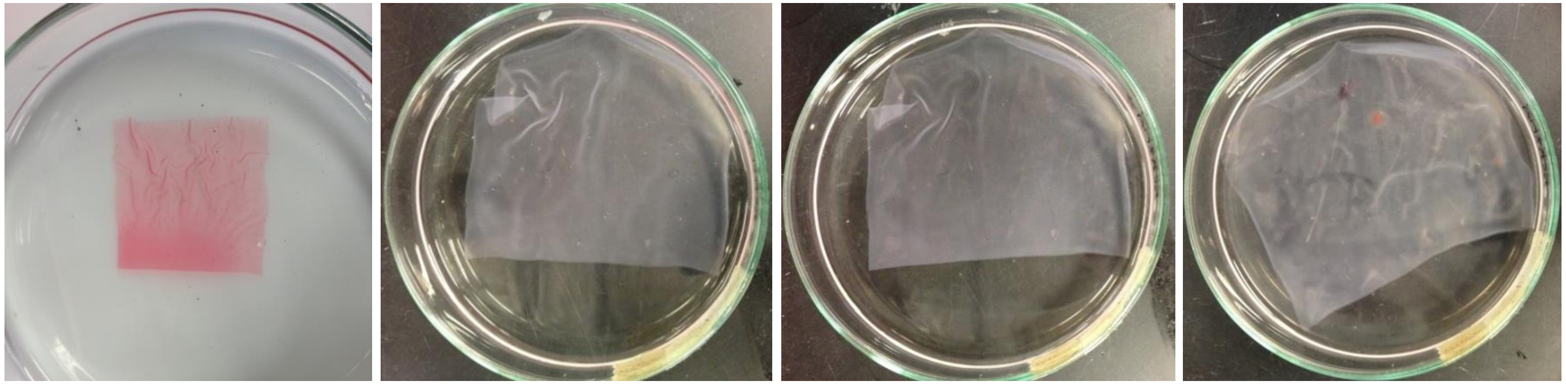
Figure 4.4: Comparison of SCA25 Films



(a) Without food colouring (b) With red food colouring

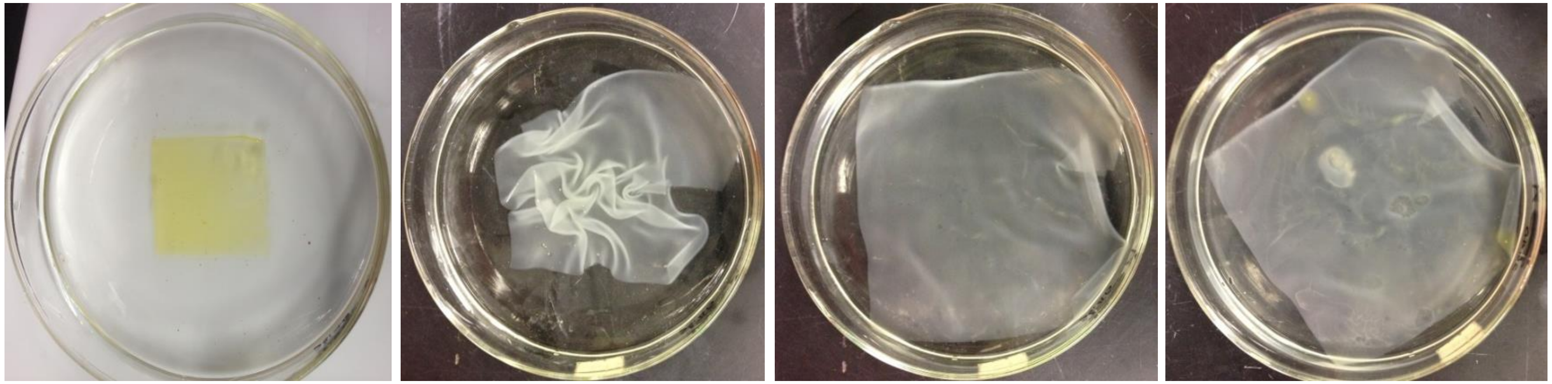
Figure 4.5: Comparison of SCA10 Film Squares

4.2.1 Swelling/Disintegration Test



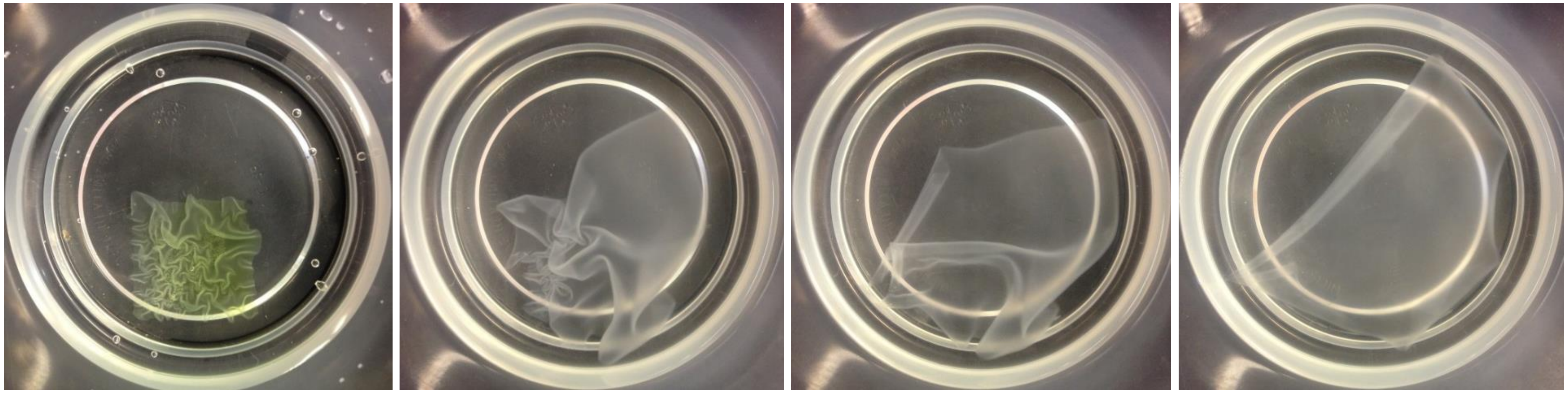
(a) Upon immersion *(b) 1 day of immersion* *(c) 2 days of immersion* *(d) 1 week of immersion*

Figure 4.6: SCA10 Swelling Behaviour



(a) Upon immersion *(b) 1 day of immersion* *(c) 2 days of immersion* *(d) 1 week of immersion*

Figure 4.7: SCA15 Swelling Behaviour



(a) Upon immersion *(b) 1 day of immersion* *(c) 2 days of immersion* *(d) 1 week of immersion*

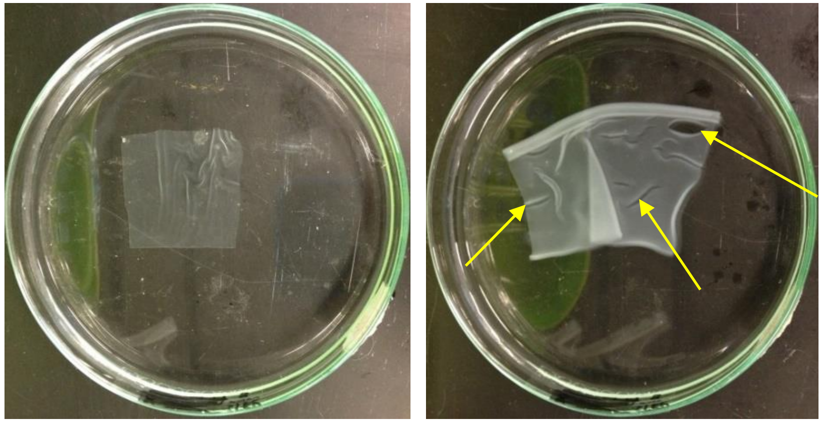
Figure 4.8: SCA20 Swelling Behaviour

(a) Upon immersion *(b) 1 day of immersion* *(c) 2 days of immersion* *(d) 1 week of immersion*

Figure 4.9: SCA25 Swelling Behaviour

(a) Upon immersion *(b) 1 day of immersion* *(c) 2 days of immersion* *(d) 1 week of immersion*

Figure 4.10: SCA30 Swelling Behaviour



(a) Upon immersion *(b) 1 day of immersion*

Figure 4.11: SCA0 Swelling Behaviour

All film squares were intact upon immersion in water. After being immersed for a few days, the film squares still retained their shape but had swollen and expanded in size, as shown in ***Figures 4.6 to 4.10***. This swelling behaviour is due to water absorption. More information on water absorption is discussed in ***Section 4.3.1***.

Figure 4.11 shows the swelling behaviour of an SCA0 film square. In ***Figure 4.11(b)***, small slits and punctures can be seen on the film (indicated by yellow arrows). This film square has also expanded at a noticeably lower degree as compared to the other films. Hereafter, the SCA0 film will be disregarded as it begins to degenerate in water over a short period of time.

4.2.2 Water Uptake Test

The percentage water uptake is calculated according to the following equations:

$$\text{Water uptake (g)} = \text{Weight of film (g)} - \text{Dry weight of film (g)}$$

$$\text{Water uptake (\%)} = \frac{\text{Water uptake (g)}}{\text{Dry weight of film (g)}} \times 100$$

24-hour Samples

Table 4.3 below shows the averaged data collected daily for films cast for **24 hours**. The full set of data can be found in ***Appendix A***.

Table 4.3: Water Uptake Test Data for 24-hour Samples

SCA10						
Dry weight of film = 0.2791 g						
Day	0	1	2	3	4	8
Weight of film (g)	0.2791	7.0006	7.0194	7.6916	8.3189	10.3162
Water uptake (g)	0	6.7215	6.7403	7.4125	8.0398	10.0371
Water uptake (%)	**0**	**2408.26**	**2415.01**	**2655.85**	**2880.60**	**3596.25**

SCA15						
Dry weight of film = 0.3515 g						
Day	0	1	2	3	4	8
Weight of film (g)	0.3515	6.5663	6.4878	6.4971	7.3685	10.3460
Water uptake (g)	0	6.2148	3.1363	6.1456	7.0170	9.9945
Water uptake (%)	**0**	**1768.09**	**1745.76**	**1748.38**	**1996.30**	**2843.38**

SCA20					
Dry weight of film = 0.2516 g					
Day	0	1	2	3	7
Weight of film (g)	0.2516	4.4071	4.7384	4.3806	3.8928
Water uptake (g)	0	4.1155	4.4868	4.1390	3.6412
Water uptake (%)	**0**	**1651.61**	**1783.29**	**1645.05**	**1447.21**

SCA25					
Dry weight of film = 0.2680 g					
Day	0	1	2	3	7
Weight of film (g)	0.2680	4.4694	4.9096	4.6197	6.4231
Water uptake (g)	0	4.2014	4.6416	4.3517	6.1551
Water uptake (%)	**0**	**1567.69**	**1731.93**	**1623.76**	**2296.69**

SCA30					
Dry weight of film = 0.2577 g					
Day	0	1	2	5	6
Weight of film (g)	0.2577	3.9581	3.8654	4.1523	4.1884
Water uptake (g)	0	3.7004	3.6077	3.8946	3.9307
Water uptake (%)	**0**	**1435.93**	**1399.96**	**1511.29**	**1525.30**

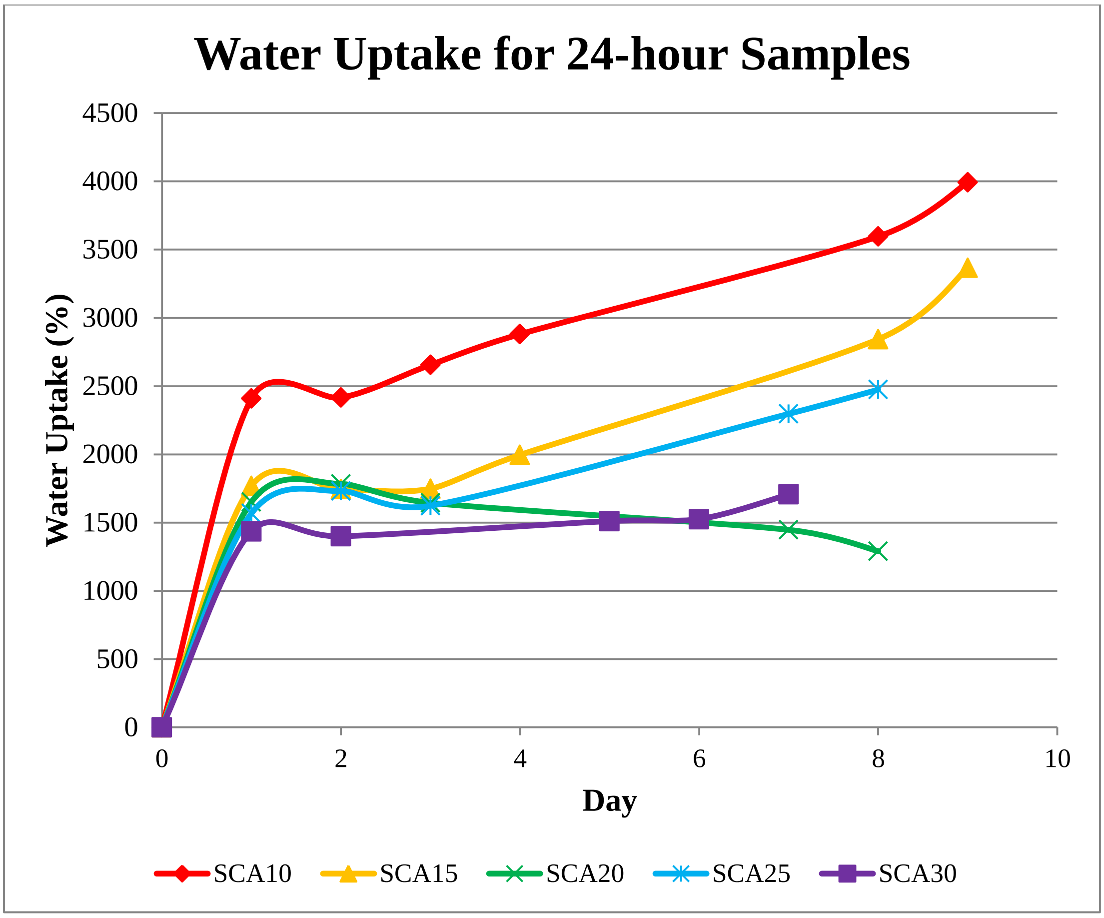


Figure 4.12: Graph of Water Uptake over Time for 24-hour Samples

The graph in ***Figure 4.12*** is plotted based on ***Table 4.3*** and shows the percentage water uptake with respect to the number of days all the 24-hour samples were immersed in water. SCA10, SCA15, SCA25 and SCA30 films appear to have increasing water uptake even after one week of immersion. The SCA20 film, however, began to dissolve and decrease in weight continuously after 2 days of immersion due to unknown reasons. Omitting SCA20 data, the SCA10 film recorded the highest percentage of water uptake whereas the SCA30 film recorded the lowest percentage of water uptake.

72-hour Samples

Table 4.4 below shows the averaged data collected daily for films cast for **72 hours**. The full set of data can be found in ***Appendix B***.

Table 4.4: Water Uptake Test Data for 72-hour Samples

SCA10				
Dry weight of film = 0.3184 g				
Day	0	1	5	6
Weight of film (g)	0.3184	6.2510	13.3869	15.5722
Water uptake (g)	0	5.9326	13.0685	15.2538
Water uptake (%)	**0**	**1863.24**	**4104.44**	**4790.77**
SCA15				
Dry weight of film = 0.3095 g				
Day	0	1	5	6
Weight of film (g)	0.3095	5.5557	12.7954	14.0827
Water uptake (g)	0	5.2462	12.4859	13.7732
Water uptake (%)	**0**	**1695.07**	**4034.23**	**4450.15**
SCA20				
Dry weight of film = 0.1885 g				
Day	0	1	5	6
Weight of film (g)	0.1885	4.8447	7.4251	7.6191
Water uptake (g)	0	4.6562	7.2366	7.4306
Water uptake (%)	**0**	**2470.13**	**3839.03**	**3941.96**
SCA25				
Dry weight of film = 0.1944 g				
Day	0	1	5	6
Weight of film (g)	0.1944	3.9466	5.6617	6.1324
Water uptake (g)	0	3.7522	5.4673	5.9380
Water uptake (%)	**0**	**1930.13**	**2812.38**	**3054.53**
SCA30				
Dry weight of film = 0.3449 g				
Day	0	1	5	6
Weight of film (g)	0.3449	4.1480	4.8859	5.3294
Water uptake (g)	0	3.8031	4.5410	4.9845
Water uptake (%)	**0**	**1102.68**	**1316.61**	**1445.20**

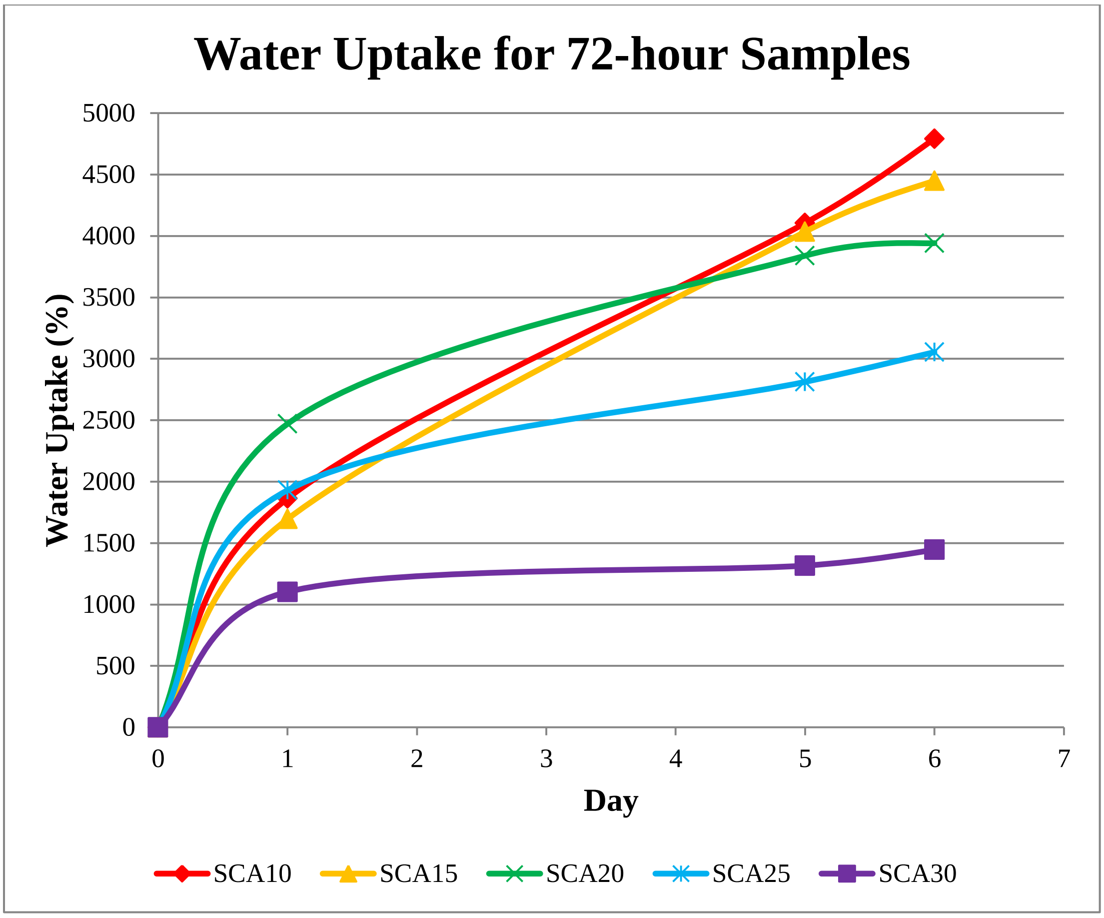


Figure 4.13: Graph of Water Uptake over Time for 72-hour Samples

The graph in ***Figure 4.13*** is plotted based on ***Table 4.4*** and shows the percentage water uptake with respect to the number of days all the 72-hour samples were immersed in water. The films have increasing water uptake with increasing citric acid content. Like the 24-hour samples, the SCA10 film recorded the highest percentage of water uptake whereas the SCA30 film recorded the lowest percentage of water uptake.

240-hour Samples

Table 4.5 below shows the averaged data collected daily for films cast for **240 hours**. The full set of data can be found in ***Appendix C***.

Table 4.5: Water Uptake Test Data for 240-hour Samples

SCA10 (Dry weight = 0.2842 g)							
Day	0	1	2	3	4	5	9
Weight of film (g)	0.2842	4.7677	5.7617	6.1734	7.6357	8.2890	8.4920
Water uptake (g)	0	4.4835	5.4775	5.8892	7.3515	8.0048	8.2079
Water uptake (%)	**0**	**1577.59**	**1927.34**	**2072.20**	**2586.74**	**2816.59**	**2888.06**
SCA15 (Dry weight = 0.3266 g)							
Day	0	1	2	3	4	5	9
Weight of film (g)	0.3266	5.3483	6.0792	6.2634	6.4392	6.6305	7.6215
Water uptake (g)	0	5.0217	5.7526	5.9368	6.1126	6.3039	7.2949
Water uptake (%)	**0**	**1537.58**	**1761.37**	**1817.76**	**1871.58**	**1930.16**	**2233.58**
SCA20 (Dry weight = 0.3015 g)							
Day	0	1	2	3	4	5	9
Weight of film (g)	0.3015	4.4328	4.8823	5.2045	5.6865	5.8200	6.1836
Water uptake (g)	0	4.1313	4.5808	4.9030	5.3850	5.5185	5.8154
Water uptake (%)	**0**	**1370.23**	**1519.34**	**1626.19**	**1786.08**	**1830.33**	**1950.95**
SCA25 (Dry weight = 0.2855 g)							
Day	0	1	2	3	4	5	9
Weight of film (g)	0.2855	3.6720	4.3238	4.7929	4.8901	5.0852	5.5907
Water uptake (g)	0	3.3865	4.0383	4.5074	4.6046	4.7997	5.3052
Water uptake (%)	**0**	**1186.15**	**1414.46**	**1578.76**	**1612.81**	**1681.16**	**1858.23**
SCA30 (Dry weight = 0.3018 g)							
Day	0	1	2	3	4	5	9
Weight of film (g)	0.3018	2.4916	4.2828	5.2573	5.2369	5.2946	5.5059
Water uptake (g)	0	2.1898	3.9810	4.9555	4.9351	4.9928	5.2041
Water uptake (%)	**0**	**725.58**	**1319.09**	**1641.98**	**1635.21**	**1654.33**	**1724.37**

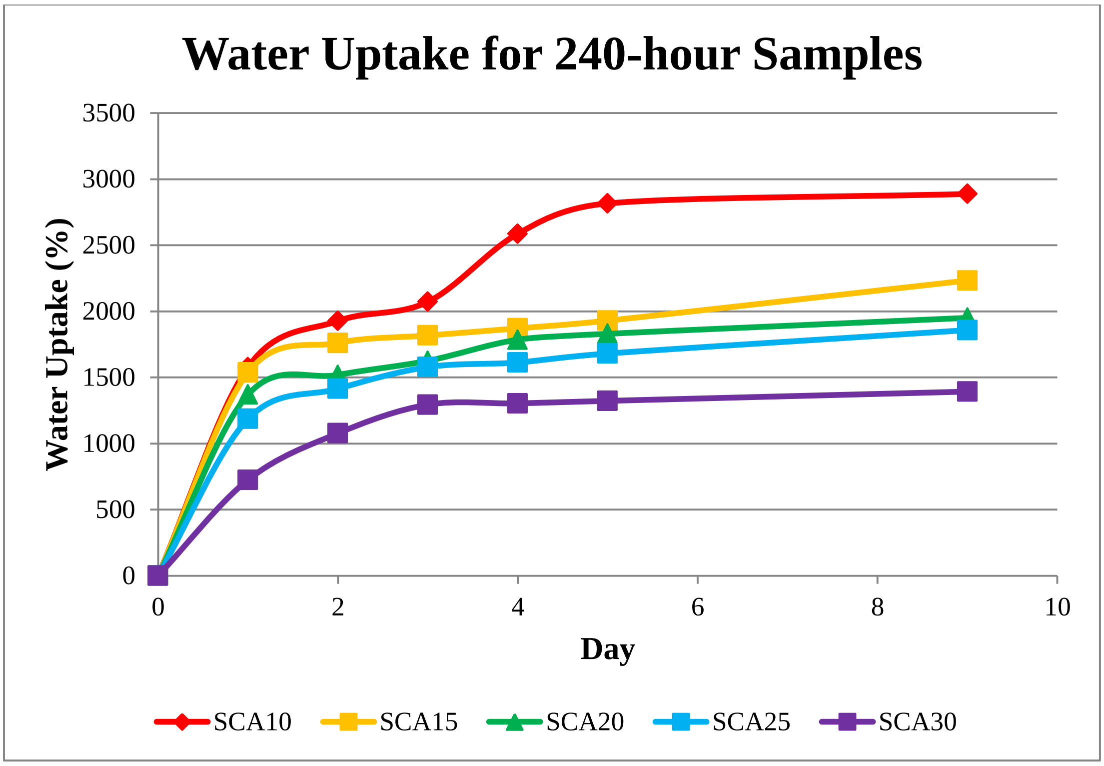


Figure 4.14: Graph of Water Uptake over Time for 240-hour Samples

The graph in ***Figure 4.14*** is plotted based on ***Table 4.5*** and shows the percentage water uptake with respect to the number of days all the 240-hour samples were immersed in water. The 240-hour samples exhibit similar trends as the 24-hour and 72-hour samples, with the SCA10 film recording the highest percentage of water uptake and the SCA30 film recording the lowest percentage of water uptake.

4.3 DATA ANALYSIS FOR CROSS-LINKED STARCH FILMS PREPARED ACCORDING TO UPDATED EXPERIMENTAL PROCEDURE

4.3.1 Swelling/Disintegration and Water Uptake Tests

The swelling/disintegration test proved that the cross-linked starch films are able to stay intact in water for a longer period as compared to the control. Not only that, the cross-linked starch films also expanded in size due to water uptake.

In order to investigate the water uptake trends of the cross-linked starch films, the water uptake test was conducted. It proved that the **cross-linked starch films absorbed less water with increasing degrees of cross-linking**.

Water uptake in the cross-linked starch films is due the molecular structure of starch, which allows limited water entry with citric acid as a cross-linker. ***Figure 4.15*** below demonstrates how water molecules fit into starch molecules with different degrees of cross-linking.

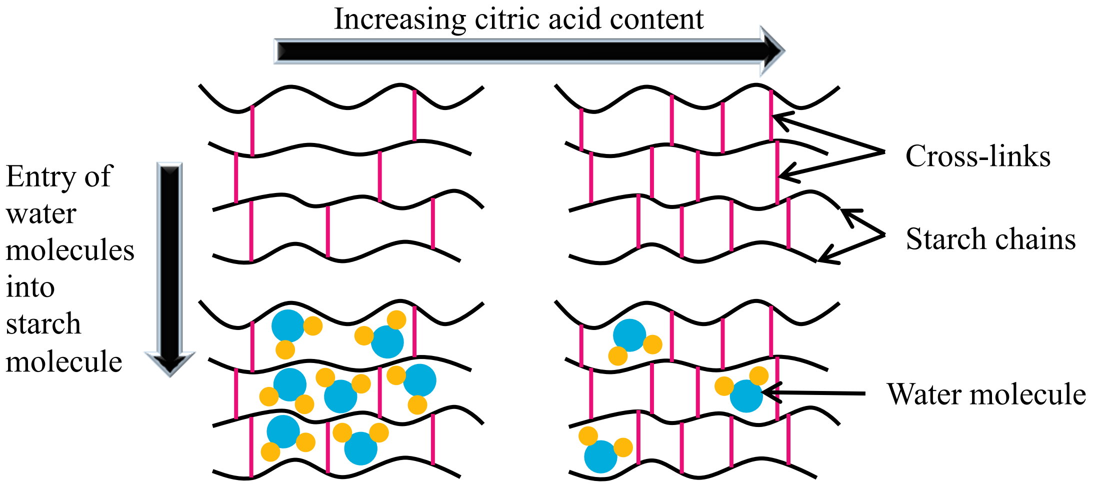


Figure 4.15: Water Absorption Mechanism in Starch Molecules

With higher citric acid content, more cross-link networks are formed in the starch molecules, which inhibit the absorption of water. This also stabilizes the film and slows its degradation rate.

4.3.2 Scanning Electron Microscopy (SEM) Images

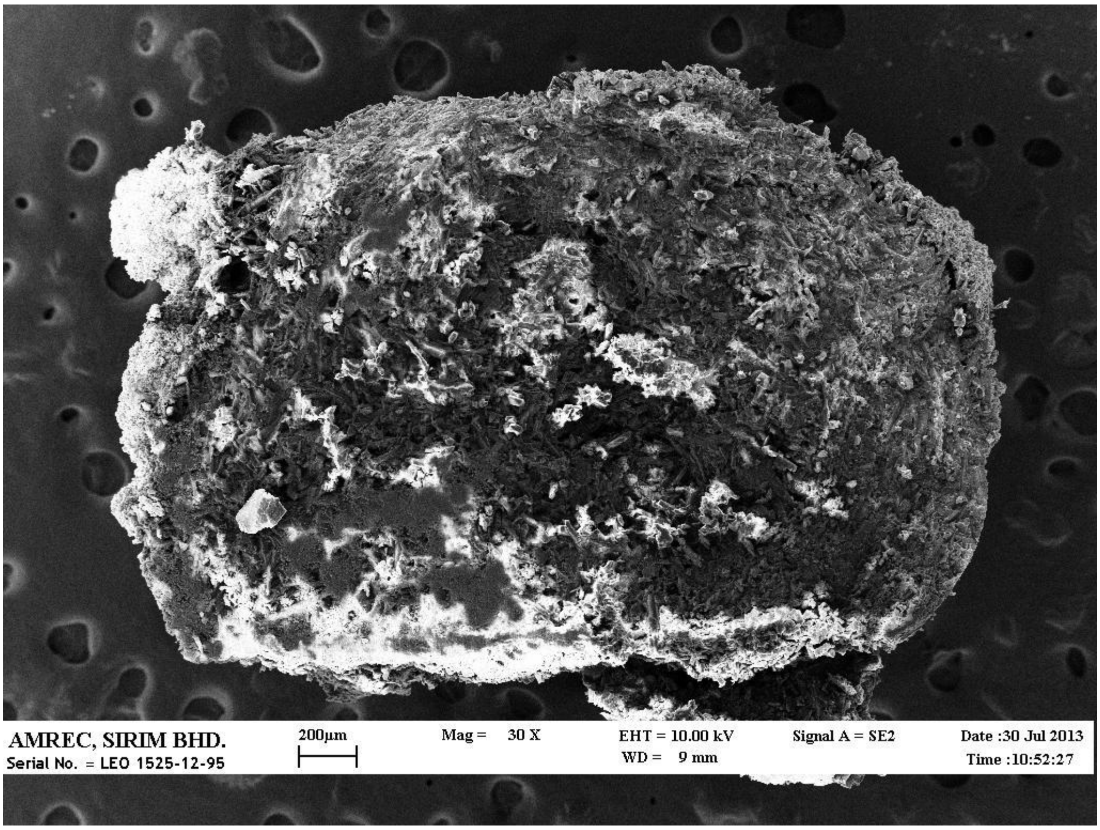


Figure 4.16: Coated Urea Prill at 30 Times Magnification

Figure 4.16 shows a coated urea prill at 30 times magnification. Considering that this is the first time citric acid cross-linked starch is used to coat urea, the coating process proved to be successful. However, since this urea prill was coated using the dip-coating method, the coating is not homogenous, causing the surface of the prill to be rough.

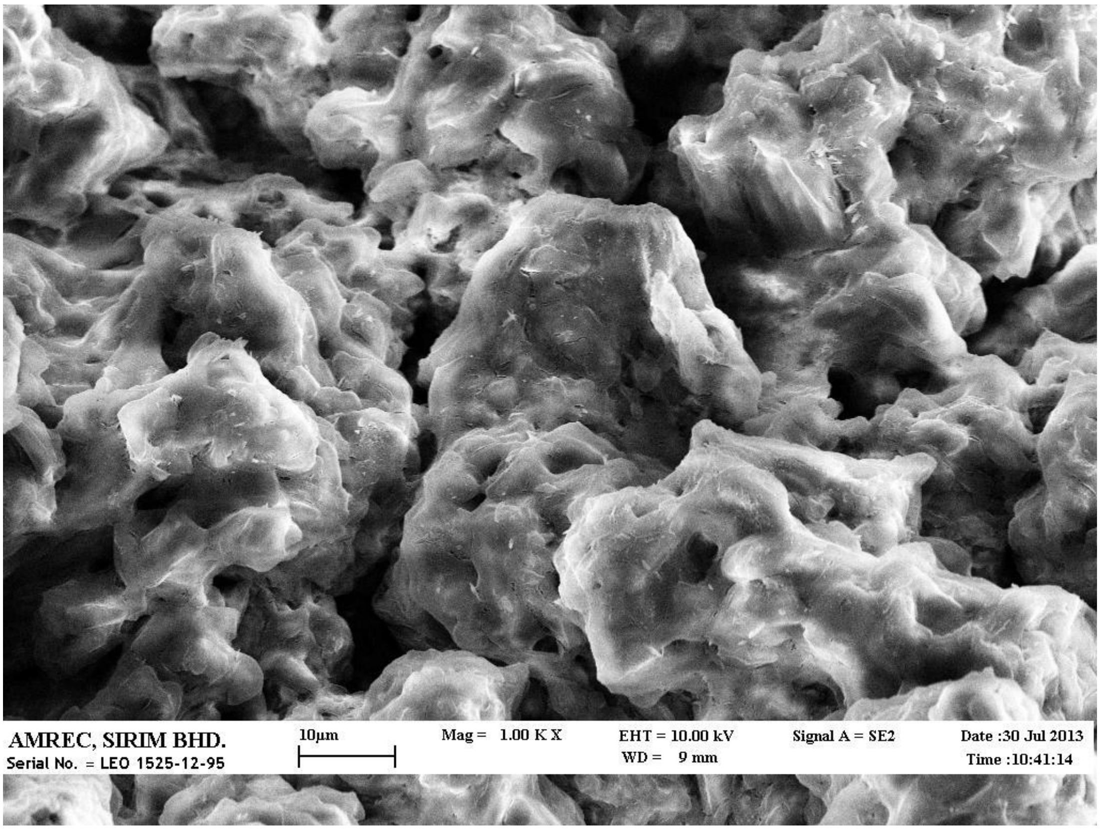


Figure 4.17: Coated Urea Prill at 1000 Times Magnification

Figure 4.17 shows a surface close-up of the coated urea prill, at a magnification of 1000 times. The light areas in the image indicate the surface coating of the urea prill, whereas the darker areas in the image indicate pores in the urea coating, which allow water entry, thus promoting swelling and water uptake.

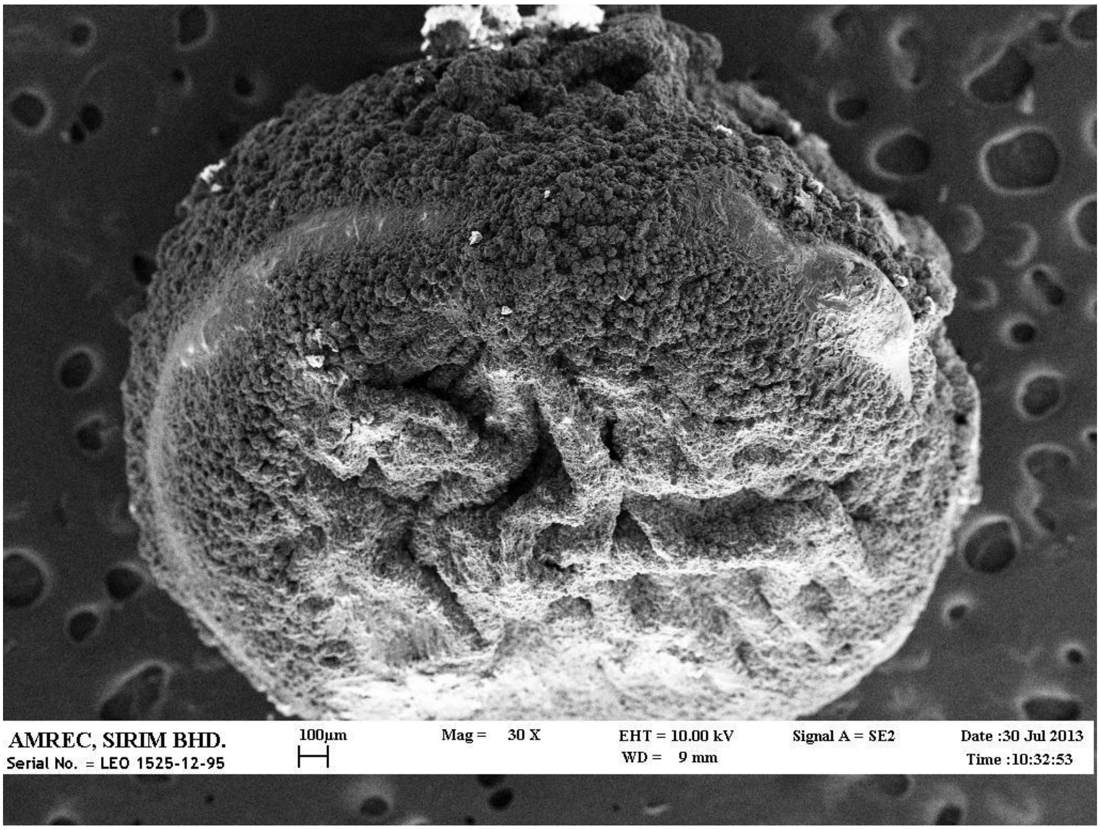


Figure 4.18: Cross Section of Coated Urea Prill at 30 Times Magnification

Figure 4.18 shows the cross section of a coated urea prill which was dissected into half. The magnification of its coated surface can be seen in ***Figure 4.19***.

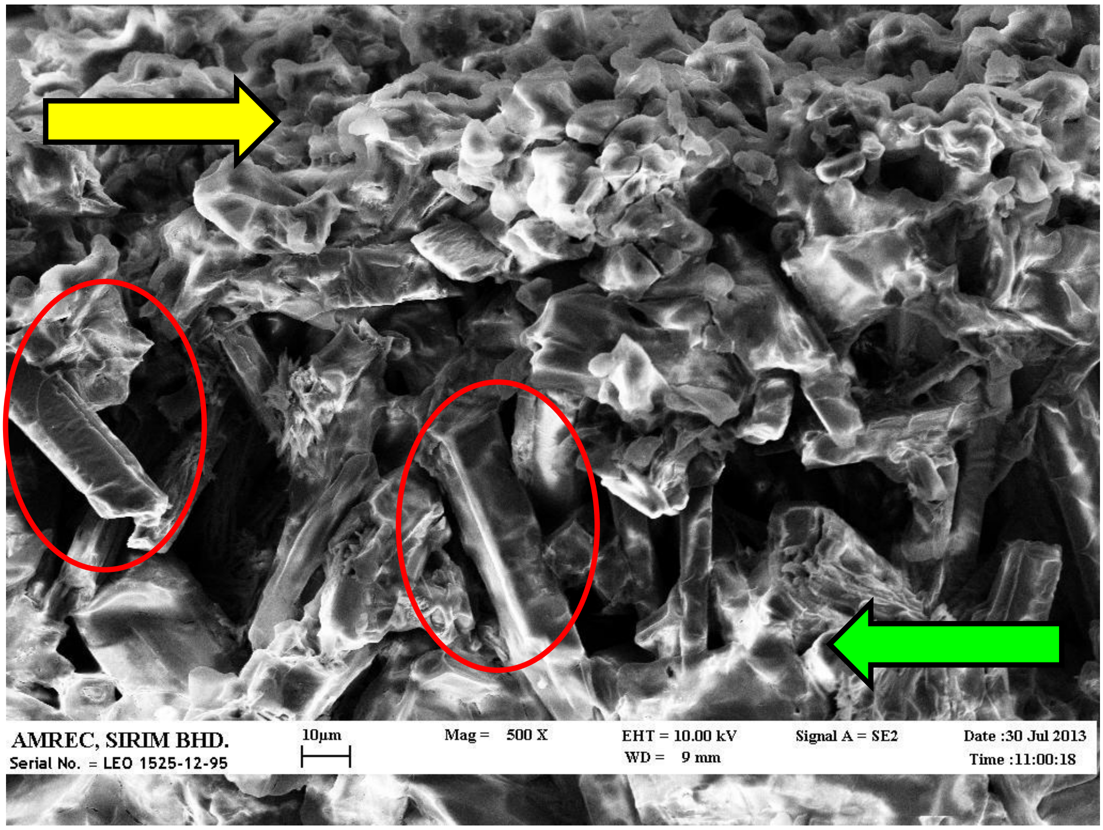


Figure 4.19: Cross Section of Coated Urea Prill at 500 Times Magnification

Figure 4.19 shows a surface close-up of the cross section of a coated urea prill, magnified by 500 times. The top half of the image (indicated by yellow arrow) is the coating whereas the bottom half of the image (indicated by green arrow) is the surface of the urea prill. The long, cuboid-shaped entities (indicated by red circles) are urea crystals at the surface boundary of the urea prill.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In conclusion, the effectiveness of citric acid as a cross-link agent used to modify native tapioca starch were studied and yielded results. The starch films were successfully cross-linked with citric acid. Based on the tests conducted on the cross-linked starch films, the **starch films cross-linked with a higher amount of citric acid exhibited lower water uptake**. This proves that the **citric acid content in cross-linked starch films can be varied** to meet the demand of various types of crops, since the water uptake rates influence the urea release mechanism in a CRF.

Also, urea coating was successfully conducted by dipping urea prills into starch solutions containing citric acid. The SEM images show that the coating adheres to the urea prill.

5.2 RECOMMENDATIONS

The cross-linked starch films have been proven to be able to coat CRFs as the films do not dissolve upon immersion in water. Perhaps more thorough coating can be achieved by using a fluidized bed instead. UV-Vis will be conducted to test the urea release from the coated urea prills.

This study can be expanded in future by substituting tapioca starch with other types of versatile starch (i.e. sago starch). Also, there are various cross-linking agents to choose from in order to produce value-added starches. Value-added starch can also be utilized for other applications, such as fish odour elimination and biomedical applications.

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APPENDICES

APPENDIX A: DAILY WATER UPTAKE TEST DATA FOR 24-HOUR SAMPLES

SCA10

Table A1: Water Uptake Test Data for 24-hour SCA10 Films

Dry weight of film = 0.2791 g				Weight of strainer = 8.4541 g					
Duration (h)	**0**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**22**
Weight of film + strainer (g)	-	14.2268	14.885	15.4707	15.6969	15.8898	15.9058	16.0357	15.5266
Weight of film (g)	0.2791	5.7727	6.4309	7.0166	7.2428	7.4357	7.4517	7.5816	7.0725
Water uptake (g)	0	5.4936	6.1518	6.7375	6.9637	7.1566	7.1726	7.3025	6.7934
Water uptake (%)	0	1968.327	2204.156	2414.009	2495.056	2564.171	2569.903	2616.446	2434.038
Duration (h)	**25**	**26**	**28**	**53**	**54**	**55**	**73**	**74**	**75**
Weight of film + strainer (g)	15.5237	15.5662	15.3306	15.8921	16.1826	16.3623	16.7063	16.6723	16.8037
Weight of film (g)	7.0696	7.1121	6.8765	7.4380	7.7285	7.9082	8.2522	8.2182	8.3496
Water uptake (g)	6.7905	6.8330	6.5974	7.1589	7.4494	7.6291	7.9731	7.9391	8.0705
Water uptake (%)	2432.999	2448.226	2363.812	2564.995	2669.079	2733.465	2856.718	2844.536	2891.616
Duration (h)	**76**	**77**	**78**	**171**	**172**	**173**	**174**	**198**	
Weight of film + strainer (g)	16.8076	16.8146	16.8332	18.5509	18.8527	18.8174	18.8603	19.878	
Weight of film (g)	8.3535	8.3605	8.3791	10.0968	10.3986	10.3633	10.4062	11.4239	
Water uptake (g)	8.0744	8.0814	8.1000	9.8177	10.1195	10.0842	10.1271	11.1448	
Water uptake (%)	2893.013	2895.521	2902.186	3517.628	3625.761	3613.114	3628.484	3993.121	

SCA15

Table A2: Water Uptake Test Data for 24-hour SCA15 Films

Dry weight of film = 0.3515 g	Weight of strainer = 8.5855 g								
Duration (h)	**0**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**22**
Weight of film + strainer (g)	-	14.6772	15.2302	15.1593	15.1457	15.2257	15.1898	15.3207	15.2661
Weight of film (g)	0.3515	6.0917	6.6447	6.5738	6.5602	6.6402	6.6043	6.7352	6.6806
Water uptake (g)	0	5.7402	6.2932	6.2223	6.2087	6.2887	6.2528	6.3837	6.3291
Water uptake (%)	0	1633.058	1790.384	1770.213	1766.344	1789.104	1778.89	1816.131	1800.597
Duration (h)	**25**	**26**	**28**	**53**	**54**	**55**	**73**	**74**	**75**
Weight of film + strainer (g)	15.1865	14.9996	15.0339	15.0263	15.1322	15.0892	15.6422	15.9553	15.9791
Weight of film (g)	6.6010	6.4141	6.4484	6.4408	6.5467	6.5037	7.0567	7.3698	7.3936
Water uptake (g)	6.2495	6.0626	6.0969	6.0893	6.1952	6.1522	6.7052	7.0183	7.0421
Water uptake (%)	1777.952	1724.78	1734.538	1732.376	1762.504	1750.27	1907.596	1996.671	2003.442
Duration (h)	**76**	**77**	**78**	**171**	**172**	**173**	**174**	**198**	
Weight of film + strainer (g)	16.0202	16.0475	16.0797	18.7179	18.9308	19.0745	19.0027	20.7701	
Weight of film (g)	7.4347	7.4620	7.4942	10.1324	10.3453	10.4890	10.4172	12.1846	
Water uptake (g)	7.0832	7.1105	7.1427	9.7809	9.9938	10.1375	10.0657	11.8331	
Water uptake (%)	2015.135	2022.902	2032.063	2782.617	2843.186	2884.068	2863.642	3366.458	

SCA20

Table A3: Water Uptake Test Data for 24-hour SCA20 Films

Dry weight of film = 0.2516 g			Weight of strainer = 8.4456 g				
Duration (h)	**0**	**1**	**2**	**3**	**4**	**26**	**27**
Weight of film + strainer (g)	-	12.5195	12.6845	12.9542	13.2524	13.2575	13.3819
Weight of film (g)	0.2516	4.0739	4.2389	4.5086	4.8068	4.8119	4.9363
Water uptake (g)	0	3.8223	3.9873	4.257	4.5552	4.5603	4.6847
Water uptake (%)	0	1519.197	1584.777	1691.971	1810.493	1812.52	1861.963
Duration (h)	**28**	**47**	**48**	**49**	**50**	**51**	
Weight of film + strainer (g)	13.4102	12.9628	12.9074	12.9447	12.9833	12.7371	
Weight of film (g)	4.9646	4.5172	4.4618	4.4991	4.5377	4.2915	
Water uptake (g)	4.7130	4.2656	4.2102	4.2475	4.2861	4.0399	
Water uptake (%)	1873.211	1695.39	1673.37	1688.196	1703.537	1605.684	
Duration (h)	**52**	**145**	**146**	**147**	**148**	**172**	
Weight of film + strainer (g)	12.6795	12.8223	12.4445	12.1749	11.9118	11.9445	
Weight of film (g)	4.2339	4.3767	3.9989	3.7293	3.4662	3.4989	
Water uptake (g)	3.9823	4.1251	3.7473	3.4777	3.2146	3.2473	
Water uptake (%)	1582.79	1639.547	1489.388	1382.234	1277.663	1290.66	

SCA25

Table A4: Water Uptake Test Data for 24-hour SCA25 Films

Dry weight of film = 0.2680 g			Weight of strainer = 8.2850 g				
Duration (h)	**0**	**1**	**2**	**3**	**4**	**26**	**27**
Weight of film + strainer (g)	-	12.2639	12.6859	12.9663	13.1015	13.2122	13.235
Weight of film (g)	0.2680	3.9789	4.4009	4.6813	4.8165	4.9272	4.95
Water uptake (g)	0	3.7109	4.1329	4.4133	4.5485	4.6592	4.682
Water uptake (%)	0	1384.664	1542.127	1646.754	1697.201	1738.507	1747.015

Duration (h)	**28**	**47**	**48**	**49**	**50**	**51**
Weight of film + strainer (g)	13.1781	13.1577	13.1898	13.0661	13.03	12.8521
Weight of film (g)	4.8931	4.8727	4.9048	4.7811	4.745	4.5671
Water uptake (g)	4.6251	4.6047	4.6368	4.5131	4.477	4.2991
Water uptake (%)	1725.784	1718.172	1730.149	1683.993	1670.522	1604.142

Duration (h)	**52**	**145**	**146**	**147**	**148**	**172**
Weight of film + strainer (g)	12.6705	14.9432	14.8293	14.5807	14.4793	15.1837
Weight of film (g)	4.3855	6.6582	6.5443	6.2957	6.1943	6.8987
Water uptake (g)	4.1175	6.3902	6.2763	6.0277	5.9263	6.6307
Water uptake (%)	1536.381	2384.403	2341.903	2249.142	2211.306	2474.142

SCA30

Table A5: Water Uptake Test Data for 24-hour SCA30 Films

Dry weight of film = 0.2577 g	Weight of strainer = 8.5123 g					
Duration (h)	**0**	**1**	**2**	**3**	**4**	**20**
Weight of film + strainer (g)	-	11.7866	11.8521	11.8652	12.0462	12.0457
Weight of film (g)	0.2577	3.2743	3.3398	3.3529	3.5339	3.5334
Water uptake (g)	0	3.0166	3.0821	3.0952	3.2762	3.2757
Water uptake (%)	0	1170.586	1196.003	1201.087	1271.323	1271.129

Duration (h)	**21**	**22**	**23**	**24**	**25**
Weight of film + strainer (g)	12.0449	12.0259	11.9951	11.9612	11.8654
Weight of film (g)	3.5326	3.5136	3.4828	3.4489	3.3531
Water uptake (g)	3.2749	3.2559	3.2251	3.1912	3.0954
Water uptake (%)	1270.819	1263.446	1251.494	1238.339	1201.164

Duration (h)	**118**	**119**	**120**	**121**	**145**
Weight of film + strainer (g)	12.0804	12.1416	12.2349	12.1884	12.6552
Weight of film (g)	3.5681	3.6293	3.7226	3.6761	4.1429
Water uptake (g)	3.3104	3.3716	3.4649	3.4184	3.8852
Water uptake (%)	1284.594	1308.343	1344.548	1326.504	1507.645

APPENDIX B: DAILY WATER UPTAKE TEST DATA FOR 72-HOUR SAMPLES

SCA10

Table B1: Water Uptake Test Data for 72-hour SCA10 Films

Dry weight of film = 0.3184 g	Weight of strainer = 8.4568 g					
Duration (h)	**0**	**1**	**2**	**3**	**4**	**19**
Weight of film + strainer (g)	-	12.3281	13.1148	13.9522	14.6523	15.0231
Weight of film (g)	0.3184	3.8713	4.6580	5.4954	6.1955	6.5663
Water uptake (g)	0	3.5529	4.3396	5.1770	5.8771	6.2479
Water uptake (%)	0	1115.861	1362.94	1625.942	1845.823	1962.28

Duration (h)	**20**	**21**	**22**	**23**	**24**
Weight of film + strainer (g)	15.2852	15.5943	15.5674	15.7034	15.8567
Weight of film (g)	6.8284	7.1375	7.1106	7.2466	7.3999
Water uptake (g)	6.5100	6.8191	6.7922	6.9282	7.0815
Water uptake (%)	2044.598	2141.677	2133.229	2175.942	2224.089

Duration (h)	**117**	**118**	**119**	**120**	**144**
Weight of film + strainer (g)	21.2240	21.6637	21.9296	22.5576	24.029
Weight of film (g)	12.7672	13.2069	13.4728	14.1008	15.5722
Water uptake (g)	12.4488	12.8885	13.1544	13.7824	15.2538
Water uptake (%)	3909.799	4047.896	4131.407	4328.643	4790.766

SCA15

Table B2: Water Uptake Test Data for 72-hour SCA15 Films

Dry weight of film = 0.3095 g	Weight of strainer = 8.3245 g					
Duration (h)	**0**	**1**	**2**	**3**	**4**	**19**
Weight of film + strainer (g)	-	12.6642	13.3225	14.7622	14.9422	13.8998
Weight of film (g)	0.3095	4.3397	4.9980	6.4377	6.6177	5.5753
Water uptake (g)	0	4.0302	4.6885	6.1282	6.3082	5.2658
Water uptake (%)	0	1302.165	1514.863	1980.032	2038.191	1701.389

Duration (h)	**20**	**21**	**22**	**23**	**24**
Weight of film + strainer (g)	13.8589	13.8068	13.8950	13.8386	13.8121
Weight of film (g)	5.5344	5.4823	5.5705	5.5141	5.4876
Water uptake (g)	5.2249	5.1728	5.2610	5.2046	5.1781
Water uptake (%)	1688.174	1671.341	1699.838	1681.616	1673.053

Duration (h)	**117**	**118**	**119**	**120**	**144**
Weight of film + strainer (g)	20.2698	21.2086	21.3483	21.6530	22.4072
Weight of film (g)	11.9453	12.8841	13.0238	13.3285	14.0827
Water uptake (g)	11.6358	12.5746	12.7143	13.019	13.7732
Water uptake (%)	3759.548	4062.876	4108.013	4206.462	4450.145

SCA20

Table B3: Water Uptake Test Data for 72-hour SCA20 Films

Dry weight of film = 0.1885 g					Weight of strainer = 8.5864 g					
Duration (h)	**0**	**1**	**2**	**3**	**4**	**97**	**98**	**99**	**100**	**124**
Weight of film + strainer (g)	-	12.1027	13.6456	13.9761	14.0000	15.8157	16.1400	15.9994	16.0908	16.2055
Weight of film (g)	0.1885	3.5163	5.0592	5.3897	5.4136	7.2293	7.5536	7.4130	7.5044	7.6191
Water uptake (g)	0	3.3278	4.8707	5.2012	5.2251	7.0408	7.3651	7.2245	7.3159	7.4306
Water uptake (%)	0	1765.411	2583.926	2759.257	2771.936	3735.172	3907.215	3832.626	3881.114	3941.963

SCA25

Table B4: Water Uptake Test Data for 72-hour SCA25 Films

Dry weight of film = 0.1944 g					Weight of strainer = 8.5597 g					
Duration (h)	**0**	**1**	**2**	**3**	**4**	**97**	**98**	**99**	**100**	**124**
Weight of film + strainer (g)	-	12.1369	12.4947	12.6836	12.7099	14.2507	14.1707	14.2043	14.2598	14.6921
Weight of film (g)	0.1944	3.5772	3.9350	4.1239	4.1502	5.6910	5.6110	5.6446	5.7001	6.1324
Water uptake (g)	0	3.3828	3.7406	3.9295	3.9558	5.4966	5.4166	5.4502	5.5057	5.9380
Water uptake (%)	0	1740.123	1924.177	2021.348	2034.877	2827.469	2786.317	2803.601	2832.15	3054.527

SCA30

Table B5: Water Uptake Test Data for 72-hour SCA30 Films

Dry weight of film = 0.3449 g					Weight of strainer = 8.4266 g					
Duration (h)	**0**	**1**	**2**	**3**	**4**	**97**	**98**	**99**	**100**	**124**
Weight of film + strainer (g)	-	11.9068	12.6847	12.8921	12.8149	13.2682	13.3769	13.2978	13.3071	13.7560
Weight of film (g)	0.3449	3.4802	4.2581	4.4655	4.3883	4.8416	4.9503	4.8712	4.8805	5.3294
Water uptake (g)	0	3.1353	3.9132	4.1206	4.0434	4.4967	4.6054	4.5263	4.5356	4.9845
Water uptake (%)	0	909.0461	1134.59	1194.723	1172.34	1303.769	1335.286	1312.351	1315.048	1445.202

APPENDIX C: DAILY WATER UPTAKE TEST DATA FOR 240-HOUR SAMPLES

SCA10

Table C1: Water Uptake Test Data for 240-hour SCA10 Films

Dry weight of film = 0.2842 g			Weight of strainer = 8.3537 g				
Duration (h)	**0**	**1**	**4**	**21**	**22**	**24**	**25**
Weight of film + strainer (g)	-	11.7564	12.8574	13.5866	13.8155	13.5911	13.6507
Weight of film (g)	0.2842	3.4027	4.5037	5.2329	5.4618	5.2374	5.2970
Water uptake (g)	0	3.1185	4.2195	4.9487	5.1776	4.9532	5.0128
Water uptake (%)	0	1097.29	1484.69	1741.27	1821.82	1742.857	1763.83
Duration (h)	**26**	**27**	**28**	**29**	**44**	**47**	**48**
Weight of film + strainer (g)	13.7568	13.9484	14.3353	13.9938	14.4878	14.3218	14.4285
Weight of film (g)	5.4031	5.5947	5.9816	5.6401	6.1341	5.9681	6.0748
Water uptake (g)	5.1189	5.3105	5.6974	5.3559	5.8499	5.6839	5.7906
Water uptake (%)	1801.16	1868.58	2004.72	1884.55	2058.37	1999.97	2037.51
Duration (h)	**49**	**74**	**75**	**76**	**95**	**96**	**97**
Weight of film + strainer (g)	14.5271	15.5081	15.4808	15.7951	16.5363	16.6268	16.6523
Weight of film (g)	6.1734	7.1544	7.1271	7.4414	8.1826	8.2731	8.2986
Water uptake (g)	5.8892	6.8702	6.8429	7.1572	7.8984	7.9889	8.0144
Water uptake (%)	2072.20	2417.38	2407.78	2518.37	2779.17	2811.01	2819.99
Duration (h)	**98**	**99**	**100**	**193**	**194**	**195**	
Weight of film + strainer (g)	16.8006	16.4692	16.6485	16.7825	16.7936	16.9612	
Weight of film (g)	8.4469	8.1155	8.2948	8.4288	8.4399	8.6075	
Water uptake (g)	8.1627	7.8313	8.0106	8.1446	8.1557	8.3233	
Water uptake (%)	2872.167	2755.559	2818.649	2865.799	2869.704	2928.677	

SCA15

Table C2: Water Uptake Test Data for 240-hour SCA15 Films

Dry weight of film = 0.3266 g				Weight of strainer = 8.6959 g			
Duration (h)	**0**	**1**	**4**	**21**	**22**	**24**	**25**
Weight of film + strainer (g)	-	13.0015	13.7683	14.4366	14.4928	14.522	14.65
Weight of film (g)	0.2842	4.3056	5.0724	5.7407	5.7969	5.8261	5.9541
Water uptake (g)	0	3.979	4.7458	5.4141	5.4703	5.4995	5.6275
Water uptake (%)	0	1218.31	1453.092	1657.716	1674.923	1683.864	1723.056
Duration (h)	**26**	**27**	**28**	**29**	**44**	**47**	**48**
Weight of film + strainer (g)	14.6264	14.7406	14.7357	14.6887	14.8333	14.9243	15.002
Weight of film (g)	5.9305	6.0447	6.0398	5.9928	6.1374	6.2284	6.3061
Water uptake (g)	5.6039	5.7181	5.7132	5.6662	5.8108	5.9018	5.9795
Water uptake (%)	1715.83	1750.796	1749.296	1734.905	1779.179	1807.042	1830.833
Duration (h)	**49**	**74**	**75**	**76**	**95**	**96**	**97**
Weight of film + strainer (g)	14.9593	14.9586	14.9909	15.068	15.2934	15.3645	15.3697
Weight of film (g)	6.2634	6.2627	6.295	6.3721	6.5975	6.6686	6.6738
Water uptake (g)	5.9368	5.9361	5.9684	6.0455	6.2709	6.342	6.3472
Water uptake (%)	1817.759	1817.544	1827.434	1851.041	1920.055	1941.825	1943.417

Duration (h)	**98**	**99**	**100**	**193**	**194**	**195**
Weight of film + strainer (g)	15.2286	15.3616	15.3457	16.2142	16.3363	16.4016
Weight of film (g)	6.5327	6.6657	6.6498	7.5183	7.6404	7.7057
Water uptake (g)	6.2061	6.3391	6.3232	7.1917	7.3138	7.3791
Water uptake (%)	1900.214	1940.937	1936.069	2201.99	2239.375	2259.369

SCA20

Table C3: Water Uptake Test Data for 240-hour SCA20 Films

Dry weight of film = 0.3015 g			Weight of strainer = 8.3461 g			
Duration (h)	**0**	**1**	**24**	**25**	**26**	**27**
Weight of film + strainer (g)	-	12.7051	12.8678	12.9056	13.0568	13.1265
Weight of film (g)	0.3015	4.359	4.5217	4.5595	4.7107	4.7804
Water uptake (g)	0	4.0575	4.2202	4.258	4.4092	4.4789
Water uptake (%)	0	1345.771	1399.735	1412.272	1462.421	1485.539
Duration (h)	**28**	**29**	**44**	**47**	**48**	**49**
Weight of film + strainer (g)	13.2957	13.2904	13.4523	13.5247	13.5309	13.5854
Weight of film (g)	4.9496	4.9443	5.1062	5.1786	5.1848	5.2393
Water uptake (g)	4.6481	4.6428	4.8047	4.8771	4.8833	4.9378
Water uptake (%)	1541.658	1539.9	1593.599	1617.612	1619.668	1637.745
Duration (h)	**74**	**75**	**76**	**95**	**96**	**97**
Weight of film + strainer (g)	13.9187	14.0236	14.035	14.1001	14.1237	14.035
Weight of film (g)	5.5726	5.6775	5.6889	5.754	5.7776	5.6889
Water uptake (g)	5.2711	5.376	5.3874	5.4525	5.4761	5.3874
Water uptake (%)	1748.292	1783.085	1786.866	1808.458	1816.285	1786.866
Duration (h)	**98**	**99**	**100**	**193**	**194**	**195**
Weight of film + strainer (g)	15.2286	15.3616	15.3457	16.2142	16.3363	16.4016
Weight of film (g)	6.5327	6.6657	6.6498	7.5183	7.6404	7.7057
Water uptake (g)	6.2061	6.3391	6.3232	7.1917	7.3138	7.3791
Water uptake (%)	1900.214	1940.937	1936.069	2201.99	2239.375	2259.369

SCA25

Table C4: Water Uptake Test Data for 240-hour SCA25 Films

Dry weight of film = 0.2855 g	Weight of strainer = 8.0010 g					
Duration (h)	**0**	**1**	**24**	**25**	**26**	**27**
Weight of film + strainer (g)	-	12.2901	12.4456	12.5532	12.629	12.8607
Weight of film (g)	0.2855	4.2891	4.4446	4.5522	4.628	4.8597
Water uptake (g)	0	4.0036	4.1591	4.2667	4.3425	4.5742
Water uptake (%)	0	1402.312	1456.778	1494.466	1521.016	1602.172
Duration (h)	**28**	**29**	**44**	**47**	**48**	**49**
Weight of film + strainer (g)	13.1137	13.2428	13.3292	13.4092	13.4733	13.5042
Weight of film (g)	5.1127	5.2418	5.3282	5.4082	5.4723	5.5032
Water uptake (g)	4.8272	4.9563	5.0427	5.1227	5.1868	5.2177
Water uptake (%)	1690.788	1736.007	1766.27	1794.291	1816.743	1827.566
Duration (h)	**74**	**75**	**76**	**95**	**96**	**97**
Weight of film + strainer (g)	13.5496	13.57	13.5831	13.6174	13.6098	13.7157
Weight of film (g)	5.5486	5.569	5.5821	5.6164	5.6088	5.7147
Water uptake (g)	5.2631	5.2835	5.2966	5.3309	5.3233	5.4292
Water uptake (%)	1843.468	1850.613	1855.201	1867.215	1864.553	1901.646
Duration (h)	**98**	**99**	**100**	**193**	**194**	**195**
Weight of film + strainer (g)	13.7727	13.7903	13.8457	14.1363	14.322	14.4016
Weight of film (g)	5.7717	5.7893	5.8447	6.1353	6.321	6.4006
Water uptake (g)	5.4862	5.5038	5.5592	5.8498	6.0355	6.1151
Water uptake (%)	1921.611	1927.776	1947.18	2048.967	2114.011	2141.891

SCA30

Table C5: Water Uptake Test Data for 240-hour SCA30 Films

Dry weight of film = 0.3018 g			Weight of strainer = 8.2549 g			
Duration (h)	**0**	**1**	**24**	**25**	**26**	**27**
Weight of film + strainer (g)	-	10.8469	10.8437	10.9101	11.5664	11.6412
Weight of film (g)	0.3018	2.592	2.5888	2.6552	3.3115	3.3863
Water uptake (g)	0	2.2902	2.287	2.3534	3.0097	3.0845
Water uptake (%)	0	758.8469	757.7866	779.7879	997.2498	1022.034
Duration (h)	**28**	**29**	**44**	**47**	**48**	**49**
Weight of film + strainer (g)	11.9623	12.3343	12.4463	12.4949	12.5443	12.5777
Weight of film (g)	3.7074	4.0794	4.1914	4.24	4.2894	4.3228
Water uptake (g)	3.4056	3.7776	3.8896	3.9382	3.9876	4.021
Water uptake (%)	1128.429	1251.69	1288.801	1304.904	1321.272	1332.339
Duration (h)	**74**	**75**	**76**	**95**	**96**	**97**
Weight of film + strainer (g)	12.5706	12.5719	12.5874	12.6092	12.6137	12.6335
Weight of film (g)	4.3157	4.317	4.3325	4.3543	4.3588	4.3786
Water uptake (g)	4.0139	4.0152	4.0307	4.0525	4.057	4.0768
Water uptake (%)	1329.987	1330.417	1335.553	1342.777	1344.268	1350.828
Duration (h)	**98**	**99**	**100**	**193**	**194**	**195**
Weight of film + strainer (g)	12.6406	12.6539	12.6651	12.83	12.8637	12.8852
Weight of film (g)	4.3857	4.399	4.4102	4.5751	4.6088	4.6303
Water uptake (g)	4.0839	4.0972	4.1084	4.2733	4.307	4.3285
Water uptake (%)	1353.181	1357.588	1361.299	1415.938	1427.104	1434.228